CHEMICAL REVIEWS

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considerable pressure, while inflammation limits or limits of inflammability are regarded as those limiting mixtures within which flame will propagate through the mixture indefinitely, irrespective of whether or not pressure is developed.

It is impossible to distinguish an inflammation from an explosion by the amount of violence produced. Mixtures just within the limits of inflammability, if confined in a long tube and tested by opening one end and igniting at this open end, will propagate flame quietly and slowly through the tube (usually at a uniform speed) and the speed, for a given concentration of combustibles in air, will vary with the direction of flame propagation. This same mixture, if confined in a closed bomb of sufficient size and ignited when the gases are in motion or gentle turbulence, will propagate flame at a speed many times as fast as that in the open tube and develop pressures ranging up to 30 lb. or more per square inch   Thus the violence and pressure developed by an inflammable mixture depend upon the environment and direction of flame propagation; therefore no differentiation should, or can, be made between explosive limits and limits of inflammability.

1. Factors affecting the limits of inflammability

Only a brief discussion of the various factors affecting the limits of inflammability will be given. A more complete discussion is given in published reports (5, 6, 8). The limits are affected by the direction of flame propagation, the design, diameter, and length of the test apparatus, the temperature and pressure of the mixture at the time of ignition, the percentage of water vapor present, and indirectly by the source of ignition.

Wider limits are obtained for upward propagation of flame than for horizontal or downward propagation, therefore the risk of an explosion is greater when the mixtures are ignited from below than when ignited from above.

The limits of inflammability are widened as the diameter of the apparatus is increased, rapidly at first and then more slowly as the diameter approaches 2 in. Apparatus greater than 2 in. in diameter gives limit values very little different from those obtained with 2-in. apparatus.

The apparatus must be long enough to insure continued propagation of flame after the heat imparted to the mixture by the source of ignition has been dissipated. An apparatus 3 ft. or more in length is sufficient.

It has been found that, if the apparatus is closed when the mixtures are ignited and ignition is initiated near the closed end when the gases are in gentle turbulence, the lower limit is reduced slightly (15).

Ordinary variations of laboratory temperatures have no appreciable effect on the limits of inflammability. Elevated temperatures cause widening of the limits.

Normal variations of atmospheric pressure have no appreciable effect on the limits. The effect of high pressures on the limits is neither simple nor uniform, but is specific for each inflammable mixture. As yet, no means has been developed for predicting the effect of high pressures on the limits of inflammability for any given combustible in air. In certain cases both limits are raised, in others the limits are narrowed, and in some both limits are changed as the pressure is increased.

The normal quantity of water vapor present in atmospheres at laboratory temperatures affects the lower limit of inflammability only to a slight extent. The presence of water vapor reduces the upper limit because some of the oxygen in the mixture is displaced by the water vapor, and, since the oxygen concentration is the important factor in an upper-limits mixture, as the oxygen is lowered the amount of combustible that can be burned is decreased, and so the limit is lowered.

2. Limits of inflammability of gases and vapors

Industrial safety requires that only values for the limits of inflammability of gases and vapors in air, which are obtained in apparatus giving the widest limits, be used. Keeping the above fact in mind, tabulations of the limits of inflammability of combustible gases and vapors have been made and are given in tables 1, 2, and 3. Values reported in the literature that were obtained in small apparatus and those in which the direction of flame propagation was other than upward have not been used, except where no other reported values were available In some cases values reported by several investigators were found to be in good agreement; however, only one reference has been given.

The ratios between the amount of combustible in the limit mixtures and the amount of combustible required for theoretical complete combustion with air and the relationship between the amounts of combustible in the limit mixtures and their net heats of combustion are given.

Burgess and Wheeler (3) first showed that there was a definite relationship between the calorific value of the combustible and its lower limit of inflammability; that is, the calorific values of the pure paraffin hydrocarbons times their lower limits of inflammability were a constant and that a lower-limit mixture of any of the paraffin hydrocarbons with air on combustion liberates the same amount of heat. Most of the "hot wire" combustible-gas indicators operate on this principle.

Some time later Thornton (34) announced that the upper limit bears a direct relation to the amount of oxygen needed for perfect combustion (theoretical complete combustion). He stated that in the case of paraffins the upper limit contained twice as great a volume of gas as the mixture for perfect combustion, acetylene and carbon disulfide three times the volume, hydrogen four times, and carbon monoxide six times the volume.

TABLE 1

Limits of inflammability of hydrocarbons in air

(1) TYPE	(2) NAME	(3) FORMULA	(4) LIMITS OF INFLAMMABILITY, PER CENT BY VOLUME — Lower	(5) Upper	(6) PER CENT COMBUSTIBLE IN AIR MIXTURE FOR THEORETICAL COMPLETE COMBUSTION	(7) RATIO OF LOWER LIMIT TO P C C † = COLUMN 4 ÷ COLUMN 6	(8) RATIO OF UPPER LIMIT TO P C C = COLUMN 5 ÷ COLUMN 6	(9) NET HEAT OF COMBUSTION, IN KG-CAL PER MOLE	(10) LOWER LIMIT × H C ‡ = COLUMN 4 × COLUMN 9 ÷ COLUMN 9	(11) UPPER LIMIT × H C = COLUMN 5 × COLUMN 9
Paraffin hydrocarbons	Methane	CH_4	5.00(15)§	15 00(15)	9 47	0 53	1 58	191 7	958	2876
	Ethane	C_2H_6	3 22(8)	12 45(8)	5 64	0 57	2 21	336 7	1084	4192
	Propane	C_3H_8	2 37(8)	9 50(8)	4 02	0 59	2 36	484 1	1147	4599
	Butane	C_4H_{10}	1 86(8)	8 41(8)	3 12	0 60	2 70	634 4	1180	5335
	Isobutane	C_4H_{10}	1 80(17)	8 44(17)	3 12	0 58	2 71	630 6	1135	5322
	Pentane	C_5H_{12}	1 40(17)	7 80(17)	2 55	0 55	3 06	774 9	1085	6044
	Isopentane	C_5H_{12}	1 32(3)		2 55	0 52		780 1	1030	
	Hexane	C_6H_{14}	1 25(17)	6 90(17)	2 16	0 58	3 19	915 9	1145	6320
	Heptane	C_7H_{16}	1 00(31)	6 00(31)	1 87	0 53	3 21	1064 5	1065	6387
	Octane	C_8H_{18}	0 95(17)		1 65	0 58		1207 7	1147	
	Nonane	C_9H_{20}	0 83(29)		1 47	0 56		1353 0*	1123	
	Decane	$C_{10}H_{22}$	0 67(31)		1 33	0 50		1494 0	1001	
Olefins	Ethylene	C_2H_4	2 75(25)	28 60(26)	6 52	0 42	4 39	310 9	855	8892
	Propylene	C_3H_6	2 00(17)	11 10(17)	4 44	0 45	2 50	460 5	921	5112
	Butylene	C_4H_8	1 70(36)	9 00(36)	3 37	0 50	2 67	611 7	1040	5505
	Amylene	C_5H_{10}	1 60(29)		2 71	0 59		750 6	1201	
Acetylenes	Acetylene	C_2H_2	2 50(17)	80.00(36)	7 72	0.32	10 36	301 5	754	24120
Aromatics	Benzene	C_6H_6	1 41(17)	6.75(17)	2 71	0 52	2 49	750 6	1058	5067
	Toluene	C_7H_8	1 27(13)	6 75(37)	2 27	0 56	2 97	892 0	1133	6021
	o-Xylene	C_8H_{10}	1.00(31)	6.00(31)	1 95	0.51	3.08	1038 9	1039	6233

Cyclic hydrocarbons	Cyclopropane	C_3H_6	2.40[17]	10.40[17]	4 44	0.54	2 34	465.1	1116	4837
	Cyclohexane	C_6H_{12}	1 33[3]	8.35[2]	2 27	0.59	3.68	875.6	1165	7311
	Methylcyclohexane	C_7H_{14}	1.15[30]		1.95	0 59		1017 9	1171	
Terpenes	Turpentine	$C_{10}H_{16}$	0.80[31]		1.47	0 55		1385 5	1108	

* Estimated.

† p.c.c. = per cent combustible in air. Mixture for theoretical complete combustion.

‡ h.c. = net heat of combustion.

§ Superior numbers in parentheses are reference numbers.

TABLE 2

Limits of inflammability of alcohols, aldehydes, ethers, ketones, acids, and esters in air

(1) TYPE	(2) NAME	(3) FORMULA	(4) LIMITS OF INFLAMMABILITY, PER CENT BY VOLUME — Lower	(5) Upper	(6) PER CENT COMBUSTIBLE IN AIR MIXTURE FOR THEORETICAL COMPLETE COMBUSTION	(7) RATIO OF LOWER LIMIT TO P.C.C.‡ = COLUMN 4 ÷ COLUMN 6	(8) RATIO OF UPPER LIMIT TO P.C.C. = COLUMN 5 ÷ COLUMN 6	(9) NET HEAT OF COMBUSTION, IN KG-CAL PER MOLE	(10) LOWER LIMIT × H.C.‡ = COLUMN 4 × COLUMN 9	(11) UPPER LIMIT × H.C. = COLUMN 5 × COLUMN 9
Alcohols	Methyl alcohol	CH_4O	6 72[22]§	36 50[37]	12 24	0 55	2 98	149 8	1007	5468
	Ethyl alcohol	C_2H_6O	3 28[13]	18 95[38]	6 52	0 50	2 91	295 9	971	5607
	Propyl alcohol	C_3H_8O	2 55[28]		4 44	0 57		438 3	1118	
	Isopropyl alcohol	C_3H_8O	2 65[28]		4 44	0 60		432 6	1146	
	Butyl alcohol	$C_4H_{10}O$	1 70[31]		3 37	0 50		585 8	996	
	Isobutyl alcohol	$C_4H_{10}O$	1.68[28]		3 37	0 50		585 4	983	
	Amyl alcohol	$C_5H_{12}O$	1 19[28]		2 71	0 44		730.3	869	
	Isoamyl alcohol	$C_5H_{12}O$	1 20[31]		2 71	0 44		711 6	854	
	Allyl alcohol	C_3H_6O	2 40[31]		4 97	0 48		410 6	985	
Aldehydes	Acetaldehyde	C_2H_4O	3 97[37]	57 00[37]	7 72	0 51	7 38	257 8	1023	14695
	Crotonaldehyde	C_4H_6O	2 12[22]	15 50[17]	4 02	0 53	3 86	510 4	1082	7911
	Furfural	$C_5H_4O_2$	2 10[31]		4 02	0 52		538 4	1131	
	Paraldehyde	$C_6H_{12}O_3$	1 30[31]		2 71	0 48		788 1*	1025	
Ethers	Methyl ethyl ether	C_3H_8O	2 00[31]	10 10[31]	4 44	0 45	2 27	461.1	922	4657
	Diethyl ether	$C_4H_{10}O$	1 85[29]	36 50[26]	3 37	0 55	10 83	598.8	1108	21856
	Divinyl ether	C_4H_6O	1 70[14]	27 00[44]	4 02	0 42	6 72	569.1	967	15366
Ketones.	Acetone	C_3H_6O	2 55[15]	12 80[16]	4 97	0 51	2 58	395.0	1007	5056
	Methyl ethyl ketone	C_4H_8O	1 81[17]	9 50[17]	3 67	0 49	2 59	540 1	978	5131
	Methyl propyl ketone	$C_5H_{10}O$	1 55[17]	8.15[17]	2 90	0 53	2 81	682 8	1058	5565
	Methyl butyl ketone	$C_6H_{12}O$	1.22[17]	8.00[17]	2 40	0 51	3 23	831.8	1015	6654

				Mixture for theoretical complete combustion					
Acids	Acetic acid	$C_2H_4O_2$	4.05(29)		9.47	0.43		188 3	763	
	Hydrocyanic acid	HCN	5 60(22)	40 00(22)	14 34	0 39	2.79	154 4	865	6176
Esters	Methyl formate	$C_2H_4O_2$	5 05(23)	22 70(23)	9.47	0 53	2 40	212 0	1071	4812
	Ethyl formate	$C_2H_6O_2$	2 75(22)	16 40(25)	5 64	0 49	2 91	359 9	990	5902
	Methyl acetate	$C_3H_6O_2$	3 15(22)	15 60(22)	5 64	0 56	2 77	349 4	1101	5451
	Ethyl acetate	$C_4H_8O_2$	2 18(13)	11 40(27)	4 02	0 54	2 84	494 7	1078	5640
	Propyl acetate	$C_5H_{10}O_2$	2 05(7)		3.12	0 66		633 0*	1298	
	Isopropyl acetate	$C_5H_{10}O_2$	2 00(34)		5.12	0 64		638 0	1276	
	Butyl acetate	$C_6H_{12}O_2$	1.70(7)		2 55	0 67		768.4	1306	
	Amyl acetate	$C_7H_{14}O_2$	1 10(41)		2 16	0 51		968 6	1065	

* Estimated.
† p.c c. = per cent combustible in air   Mixture for theoretical complete combustion.
‡ h.c. = net heat of conbustion.
§ Superior numbers in parentheses are reference numbers.

TABLE 3

Limits of inflammability of miscellaneous combustible gases and vapors in air

(1) TYPE	(2) NAME	(3) FORMULA	(4) LIMITS OF INFLAMMABILITY, PER CENT BY VOLUME — Lower	(5) Upper	(6) PER CENT COMBUSTIBLE IN AIR MIXTURE FOR THEORETICAL COMPLETE COMBUSTION	(7) RATIO OF LOWER LIMIT TO Pct = COLUMN 4 ÷ COLUMN 6	(8) RATIO OF UPPER LIMIT TO Pct = COLUMN 5 ÷ COLUMN 6	(9) NET HEAT OF COMBUSTION, IN KG-CAL PER MOLE	(10) LOWER LIMIT × Hct = COLUMN 4 × COLUMN 9	(11) UPPER LIMIT × Hc = COLUMN 5 × COLUMN 9
Hydrogen	Hydrogen	H_2	4 00(11)§	74 20(4)	29.50	0 14	2 52	57 8	231	4289
Carbon monoxide	Carbon monoxide	CO	12 50(6)	74 20(4)	29.50	0 42	2 52	67 6	845	5016
Nitrogen compounds	Ammonia	NH_3	15 50(9)	27 00*	21 82	0 71	1 24	76.2	1181	2057
	Cyanogen	C_2N_2	6 60(1)	42 60(1)	9 47	0 70	4 50	258 3	1705	11004
	Pyridine	C_5H_5N	1 81(37)	12 40(37)	3 24	0 56	3 83	652 1	1180	8086
	Ethyl nitrate	$C_2H_5NO_3$	3 80(28)		10 68	0 36		296 0	1125	
	Ethyl nitrite	$C_2H_5NO_2$	3 01(37)	50 00(37)	8 51	0 35	5 88	306 2	922	15310
Oxides	Ethylene oxide	C_2H_4O	3 00(19)	80 00(19)	7 72	0 39	10 36	281 0	843	22480
	Propylene oxide	C_3H_6O	2 00(27)	22 00(27)	4 97	0 40	4 43			
	Dioxan oxide	$C_4H_8O_2$	1.97(24)	22 25(24)	4 02	0.49	5 53	539.8	1063	12011
	Diethyl peroxide	$C_4H_{10}O_2$	2 34(38)		3 67	0 64				
Sulfides	Carbon disulfide	CS_2	1 25(17)	50 00(37)	6 52	0 19	7 67	246 6	308	12330
	Hydrogen sulfide	H_2S	4 30(36)	45 50(36)	12 24	0 35	3 72	122 5	527	5574
	Carbon oxysulfide	COS	11.90(19)	28 50(19)	12 24	0 97	2 33	130.5	1553	3719
Chlorides	Methyl chloride	CH_3Cl	8 25(13)	18.70(13)	12 24	0 67	1.53	153 7	1268	2874
	Vinyl chloride	C_2H_3Cl	4.00(17)	21.70(17)	7 72	0.52	2 81	270 9	1084	5879
	Ethyl chloride	C_2H_5Cl	4.00(13)	14 80(13)	6 52	0.61	2.27	295.6	1182	4375

Chlorides	Amyl chloride	$C_5H_{11}Cl$	1.40[17]		2.71	0 52		731.9	1025	2874
	Dichloroethylene	$C_2H_2Cl_2$	9 70[7]	12 80[7]	9.47	1 02	1.35	224 5	2178	3973
	Ethylene dichloride	$C_2H_4Cl_2$	6.20[19]	15 90[19]	7 72	0.80	2 06	249.9	1549	
	Propylene dichloride	$C_3H_6Cl_2$	3 40[25]	14.50[25]	4.97	0.68	2.92	396.1	1347	5743
Bromides	Methyl bromide	CH_3Br	13.50[12]	14.50[12]	12 24	1 10	1.18	173 5	2342	2516
	Ethyl bromide	C_2H_5Br	6.75[12]	11.25[12]	6 52	1.04	1.73	319 4	2156	3593

* Average of several reported values

† p.c.c. = per cent combustible in air. Mixture for theoretical complete combustion.

‡ h.c. = net heat of combustion.

§ Superior numbers in parentheses are reference numbers.

Lower-limit mixtures which just failed to propagate flame contained twice the volume of oxygen needed for perfect combustion in the case of the paraffins, and thrice the volume in the case of the other gases. The values given in tables 1, 2, and 3 show that some of the predictions given by Thornton are approximately correct, while in other cases there are extremely wide variations, and that the classification is not nearly so simple as Thornton predicted.

The relationship between the calorific value of the combustibles, the oxygen required for perfect combustion, and the limits of inflammability

TABLE 4

Limits of inflammability of selected gases and vapors in air showing variation of ratios between the percentage of combustibles in the limit mixtures and that required for theoretical complete combustion and the relationship between the limits and net heats of combustion

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
		LIMITS OF INFLAMMABILITY, PER CENT BY VOLUME		PER CENT COMBUSTIBLE IN AIR MIXTURE FOR THEORETICAL COMPLETE COMBUSTION	RATIO OF LOWER LIMIT TO P C C * = COLUMN 3 ÷ COLUMN 5	RATIO OF UPPER LIMIT TO P C C = COLUMN 4 ÷ COLUMN 5	NET HEAT OF COMBUSTION, IN KG - CAL PER MOLE	LOWER LIMIT × H C † = COLUMN 3 × COLUMN 8	UPPER LIMIT × H.C = COLUMN 4 × COLUMN 8
COMBUSTIBLE	FORMULA	Lower	Upper						
Hydrogen	H_2	4.00	74 20	29.50	0 14	2 52	57 8	231	4289
Carbon disulfide	CS_2	1 25	50 00	6 52	0 19	7 67	246 6	308	12330
Acetylene	C_2H_2	2 50	80.00	7 72	0.32	10 36	301 5	754	24120
Hydrogen sulfide	H_2S	4 30	45 50	12 24	0 35	3 72	122 5	527	5574
Ethylene oxide	C_2H_4O	3 00	80 00	7.72	0 39	10 36	281 0	843	22480
Ethylene	C_2H_4	2 75	28 60	6 52	0 42	4 39	310 9	855	8892
Methane.	CH_4	5 00	15 00	9.47	0 53	1 58	191.7	958	2876
Methyl alcohol	CH_4O	6 72	36 50	12 24	0 55	2 98	149 8	1007	5468
Methyl acetate	$C_3H_6O_2$	3 15	15 60	5 64	0 56	2.77	349 4	1101	5451
Methyl chloride	CH_3Cl	8 25	18 70	12 24	0 67	1 53	153 7	1268	2874
Methyl bromide	CH_3Br	13 50	14 50	12 24	1 10	1.18	173 5	2342	2516

* p.c c. = per cent combustible in air Mixture for theoretical complete combustion.

† h c. = net heat of combustion.

was investigated and extended by White (37) to cover a number of solvent vapors. He found that for all solvents examined, except one, the lower limit for downward propagation of flame was approximately inversely proportional to the net calorific value of the vapor used. The corresponding upper limit roughly followed a similar rule, it being about 3.5 times the lower limit. He also found that the amount of oxygen available for the combustion of a vapor in its limit mixture bore a fairly constant ratio to the amount required for the perfect combustion of 1 mole of the vapor. Thus the amount of solvent in a lower-limit mixture for downward propagation of flame was 0.57 of that present in the mixture for per-

fect combustion, while the ratio for the upper-limit mixture was just under 2.

The results given in table 4 show that no general relationship of the limits of combustible gases and vapors either to the amount of oxygen required for theoretical complete combustion or to the calorific value of the gases or vapors exists, nor do they give even approximately correct results if used indiscriminately.

On the other hand, if the combustibles are classified according to types of compounds the relationship between the limits and the oxygen required for theoretical complete combustion is of value in predicting the limits of inflammability of new compounds, the limits of which have not already been determined, as will be shown later.

3. Calculation of limits of inflammability of mixtures of combustibles

The calculation of the limits of inflammability of combustible mixtures from a knowledge of the limits of each combustible in air and the percentages of each combustible present in the mixture can be done quite accurately for a great number of mixtures by the application of the so-called "mixture law."

Le Chatelier (28) first applied the law to the limits of inflammability of gases. The law states that if we have, say, separate limit combustible-air mixtures and mix them, then this mixture will also be a limit mixture. The equation for expressing this law in its simplest form is written as follows:

$$L = \frac{100}{\dfrac{P_1}{N_1} + \dfrac{P_2}{N_2} + \dfrac{P_3}{N_3} + \dfrac{P_4}{N_4}}$$

where P_1, P_2, P_3, and P_4 are the proportions of each combustible gas present in the original mixture, free from air and inerts, so that $P_1 + P_2 + P_3 + P_4 = 100$, and N_1, N_2, N_3, and N_4 are the lower limits of inflammability of each combustible in air.

As an example of the application of this law we may take a natural gas of the following composition:

HYDROCARBON PRESENT	PER CENT BY VOLUME	LOWER LIMIT
Methane	80.0	5.00
Ethane	15 0	3 22
Propane	4 0	2.37
Butane	1.0	1 86

$$\text{Lower limit} = \frac{100}{\dfrac{80.0}{5.00} + \dfrac{15.0}{3.22} + \dfrac{4.0}{2.37} + \dfrac{1.0}{1.86}} = 4.37$$

This law has been tested by Coward, Carpenter, and Payman (5) and proved to hold for hydrogen, carbon monoxide, and methane containing no inert gases in normal air. Subsequent tests made with paraffin hydrocarbons in air (8) showed that the law could also be applied to these mixtures Exceptions have been found in tests made with some inflammable gases. White (37) found that the law does not hold strictly for hydrogen–ethylene–air mixtures, acetylene–hydrogen–air mixtures, hydrogen sulfide–methane–air mixtures, and mixtures containing carbon disulfide. Also, in tests on some chlorinated hydrocarbons, Coward and Jones (7) found that the law did not hold for methane–dichloroethylene–air mixtures, and more recently it was found (12) that the law was only approximately correct for mixtures of methyl and ethyl chlorides. It is therefore apparent that the mixture law, useful when its application has been proved, cannot be applied indiscriminately, but must first be proved to hold for the gases being investigated.

Many industrial processes require the use of mixtures of various solvents in their processes, and although the limits of inflammability of the various individual constituents in the mixture may be known, it is not at all certain what the inflammability limits will be for the various mixtures. Investigations of the lower limits of inflammability of solvent mixtures have shown that where the ratios of the lower limits of the individual constituents to the amount of oxygen required for theoretical perfect combustion are about the same, the limits of mixtures of the constituents may be determined accurately by calculation. For example, the limits of mixtures of ethyl alcohol, benzene, furfural, and acetone in which the ratios range from 0.50 to 0.53 (tables 1, 2, and 3) may be calculated, and mixtures of ethyl acetate, ethyl alcohol, and toluene, whose ratios vary from 0.50 to 0.56, have been found also to give calculated results agreeing closely with experimental results (13).

At the present time, the accuracy of the above prediction has been proved only for a limited number of mixtures; however, as information on the subject is accumulated, the classification of compounds according to the ratios should be of great value in predicting and calculating the limits of inflammability of mixtures of combustible gases and vapors.

As an example to show the application of this method for predicting the limits of inflammability of combustibles whose limits have not been determined, propyl chloride may be used. The ratio of the lower limit of certain gases to that for theoretical complete combustion is as follows:

methane....	.... 0.52	methyl chloride........ ...	0.67
ethane...	0.57	ethyl chloride	0.61
propane...	. 0.59	propyl chloride. . not known	

The addition of one chlorine atom to methane has raised the ratio 0.15, while the addition of one chlorine atom to ethane has raised the ratio only 0.04. One chlorine atom added to propane should raise the ratio even less, say 0.02, thus giving a ratio of 0.61 for propyl chloride.

When propyl chloride is burned with the theoretical amount of oxygen to give complete combustion, the following reaction takes place:

$$C_3H_7Cl + 4.5O_2 \rightarrow 3CO_2 + HCl + 3H_2O$$

or with air

$$C_3H_7Cl + 21.5 \text{ air} \rightarrow 3CO_2 + HCl + 3H_2O + 17.0N_2$$
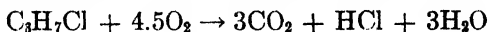
The percentage of propyl chloride in a mixture with air to give theoretical complete combustion $= \dfrac{1 \times 100}{22.5} = 4.44$ per cent. Using the ratio 0 61 for propyl chloride given above, the predicted lower limit of inflammability $= 4.44 \times 0.61 = 2.71$ per cent.

4. Limits of inflammability of complex mixtures

It is possible to calculate closely the limits of inflammability not only of certain mixtures of combustible gases and vapors in air but also of mixtures containing varying amounts of inert gases. The limits of inflammability of natural, manufactured, producer, blast furnace, automobile, and sewage gases may be calculated from a knowledge of the composition of constituents composing the gases and their limits of inflammability. The actual procedure is rather long and complicated, so only a reference to this method will be given in this report (6, 11, 20, 40).
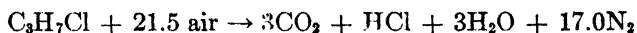
PRACTICAL MEANS OF ELIMINATING OR MINIMIZING EXPLOSIONS IN INDUSTRIAL OPERATIONS

1 Control of the oxygen content of the atmosphere

The fact that all combustible gases, vapors, mists, and pulverized solids will not burn or explode when the oxygen content is reduced below certain definite values, varying with the combustible materials under consideration, gives the safety engineer a means of definitely controlling and eliminating explosions.

The oxygen present in an explosive mixture may be reduced by direct absorption by means of special reagents, by dilution with inert gases such as nitrogen or carbon dioxide, or by combinations of these inert gases as represented by flue gas or exhaust gas from an internal-combustion engine. Flue gases made by burning fuel gas or fuel oil with the proper proportions of air and automobile exhaust gas both have a low oxygen content and are ideally suited for reducing the oxygen content of atmospheres. Carbon

dioxide compressed in cylinders, carbon tetrachloride, and dichlorodifluoro-methane have been used also for this purpose.

The critical oxygen values below which flames will not propagate or explosions take place when the reduction of the oxygen content of the atmosphere is brought about by the addition of nitrogen and carbon dioxide for several hydrocarbons are shown graphically in figure 1. The critical oxygen value for any given combustible varies with the concentration of the combustible present; however, the values given in figure 1 are minimum ones and cover all concentrations of the combustible that might be present. The relationship between concentration of combustible and the critical oxygen requirements to prevent explosions is shown to better advantage in figure 2. This graph shows the explosive areas of all possible mixtures of pentane, air, and added nitrogen or carbon dioxide. The straight line AD represents the composition of mixtures of pentane and pure air containing up to 15 per cent pentane. The limits as shown on this line are seen to be 1.4 per cent for the lower and 7.8 per cent for the upper limit. All mixtures between these limits are explosive. As nitrogen or carbon dioxide is added the oxygen concentration is lowered and, as shown, the limits are narrowed. Finally when the oxygen content is reduced to 11.7 per cent all mixtures of pentane, air, and added nitrogen become non-explosive. The mixture which will propagate flame with a minimum concentration of oxygen contains 2.10 per cent of pentane. If the atmosphere contains 5.00 per cent of pentane the graph shows that the oxygen concentration needs to be reduced to only 15.6 per cent. Although this mixture having 5.00 per cent of pentane will not explode when the oxygen content is below 15.6 per cent, the graph shows that if air is added to the mixture it becomes explosive, since addition of air shifts the composition of the mixture along the line to the left and towards the A-axis, so that the composition passes through a range of mixtures which are explosive.

The usual problem in dealing with pentane–air mixtures is to control the atmosphere so that the composition at all times is outside the explosive area bounded by BCE (when added nitrogen is used as the diluent). A graph of this type enables one to determine at a glance the explosive hazards involved. If an analysis is made of an atmosphere and it is found to contain, say, 12 per cent oxygen and 8.40 per cent pentane, this mixture, as indicated by the point J on the graph, shows at once that the mixture cannot explode until air is added; however, if the equipment is to be taken out of service and it is desired to do so without possibility of explosions, the atmosphere must be altered so as to pass around the explosive area. It becomes necessary to alter the composition of the atmosphere until it falls into the area to the left of the line AEF, and in no case should it
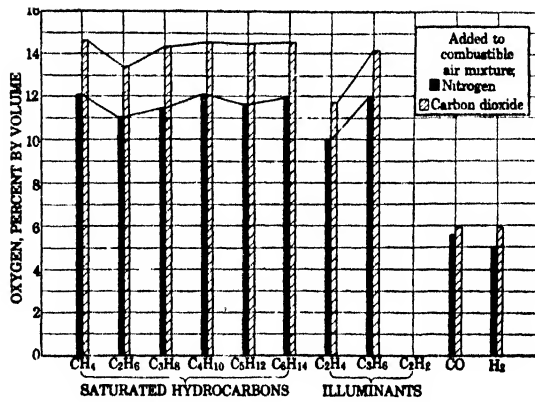
FIG 1 Per cent oxygen by volume in gas mixtures below which explosions are prevented at ordinary temperatures and pressures.
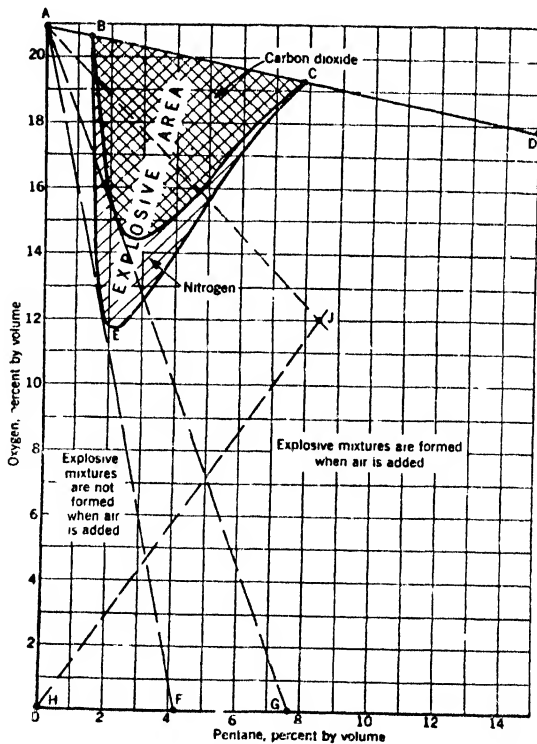

FIG. 2. Explosibility of mixtures of pentane, air, added nitrogen, and carbon dioxide

fall into the explosive area indicated. It is not necessary to reduce the oxygen content to zero to pass safely from the composition given by point J to atmospheres of the composition given by any point to the left of the line AEF. Nitrogen can be added until the oxygen content is reduced to below 4.6 per cent, thus shifting the composition along the line JH and reducing the pentane content to a value of 3.3 per cent or less, until it passes into the area to the left of the line AEF. The composition of the atmosphere now is such that it cannot be made explosive, no matter how much air is added, because a line drawn from any point in this area to A will not pass through the explosive area. Air can then be added to the equipment and the combustibles swept out without any danger of explosions. The graph given holds only for pentane, and graphs of a similar type must be constructed for each hydrocarbon concerned.

2. Carrying out operations so that the percentages of combustibles present are outside the limits of inflammability

Processes that necessitate the use of combustible gases or vapors should be carried out wherever possible under conditions in which the atmospheres are outside the limits of inflammability of the materials used. If possible, the concentrations should be kept below the lower limit of inflammability, because under these conditions if air finds its way into the mixture, there is no danger of explosions. If the concentration of combustibles must be above the lower limit of inflammability, then it is advisable to raise the concentration until the combustibles present are above the upper limit. No explosion hazards will result while the atmospheres are above the upper limit; the danger arises when additional air finds its way into the mixture, and this usually occurs when the process is started up or closed down.

If combustible liquids are used the explosion hazards may be controlled by regulation of the temperature, and in turn the vapor pressures should be so regulated that the atmosphere is either above or below the limits of inflammability. In the application of this method of control the limits of inflammability of the vapor in air and the vapor pressures of the material over the temperature range to be used must be known. The application of this method to a gasoline is given in figure 3. The lower limit of inflammability of the gasoline in air is 1.40 and the upper limit 6.90 per cent by volume; then at 1 atm. of pressure the gasoline must have a vapor pressure of 10.5 mm. of mercury to give a lower-limit and 52.5 mm. to give an upper-limit mixture. The two horizontal lines enclose the limits within which inflammable mixtures are produced, and the intersections of these lines with the vapor pressure curve give the range of vapor pressures that can produce inflammable mixtures. The corresponding temperatures in this particular case are 4°F. and 77°F. The graph shows that this

gasoline should be used at temperatures either below 4°F. or above 77°F., if the process is to be carried out under conditions where explosive mixtures will not be present.

If combustible liquids or mixtures of which the vapor pressures are not known are used in a process, the temperature range over which explosive mixtures may be present may be easily determined by means of the simple apparatus shown in figure 4. Explosion tube D is 2.5 cm. (1 in.) in diameter and 20 cm. (8 in.) long. E indicates the electrodes across which sparks generated from a transformer M and induction coil N are passed when a test of the explosibility of the atmosphere in tube D is desired. H and H′ are mercury seals through which contact is made between the electrodes and the induction coil N. The explosion tube D is immersed in a liquid
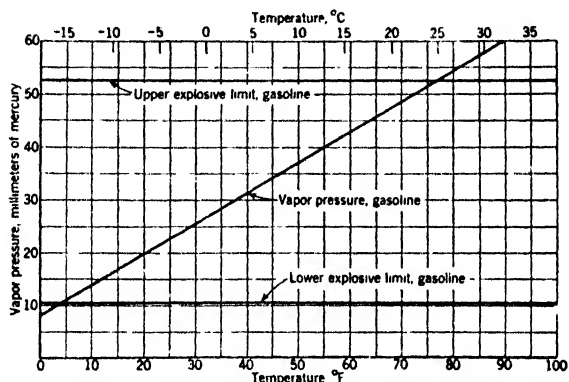
FIG. 3 Relationship between limits of inflammability and vapor pressure of a combustible liquid

bath, C, kept at uniform temperature by stirrer L, and heated to the desired temperature by burner O. K is a thermometer for recording the temperature of the bath.

To determine the temperature range over which a combustible liquid gives explosive mixtures, the combustible liquid is poured into D until the level is about 2 cm. (0.8 in.) below the electrodes, and a cork R, having an opening as shown, is placed in the top of explosion tube D. Air is turned on and adjusted to give at the start three bubbles per second, as indicated by bubbler A. The air is then passed through tower B containing a drying agent, and thence through the glass coil G in the bath to bring the air to the temperature of the bath before it enters the combustible liquid F in explosion tube D. Air is passed through the liquid at the rate given for 5 minutes at a given temperature, and a test for explosibility is made by removing cork R and causing sparks to pass at the elec-

trodes (E). If the combustible liquid gives an explosive mixture with air at the temperature tested, flame will pass up the tube and out the top. Tests are continued by the method of trial and error until a minimum temperature is obtained at which flame carries from the electrodes upward through the tube. The temperature is then kept constant and the rate of air flow changed until a rate is found which gives the lowest temperature that causes inflammation of the mixture in the tube. The temperature of the bath is then raised and the temperature at the upper-limit mixtures is ascertained in a similar manner.
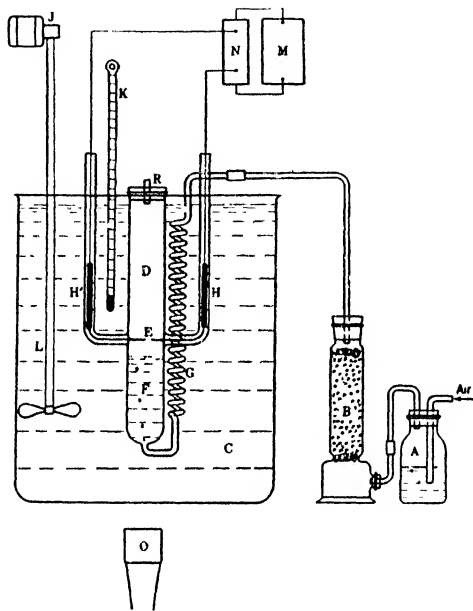
FIG 4. Apparatus for determining the explosive range of high-boiling hydrocarbons

The limits of inflammability of combustible liquids may be determined rather closely in the apparatus described, provided the vapor pressures of the liquids tested are accurately known. To obtain the limits, the vapor pressure of the liquid at the temperature at which flame is propagated is divided by the barometric pressure at the time of the experiment and multiplied by 100. Tests made both in the apparatus described and in large-scale apparatus have shown approximate agreement.

3. The use of less inflammable combustibles

Wherever possible, solvents or other materials with the least inflammable characteristics should be used. Those materials should be chosen which

have, at the temperatures used, vapor pressures that give atmospheres that are not explosive. When this cannot be done the use of chlorinated hydrocarbons should be considered. Table 5 shows how a combustible gas which has one or more hydrogen atoms replaced by chlorine gives resulting materials with reduced explosive characteristics.

Methane becomes highly explosive when mixed with the proper proportions of air. While methyl chloride does not produce as violent explosions as methane-air mixtures, nevertheless explosions of this substance in air may do considerable damage. Methylene chloride is entirely safe when mixed with air at ordinary temperatures and pressures; however, when mixed with pure oxygen in the right proportions, it becomes highly explosive. Chloroform has no explosive properties. Carbon tetrachloride is entirely non-explosive with air in any proportions, and is used to good advantage in the preparation of non-combustible and non-explosive safety

TABLE 5

Effect of substitution of chlorine atoms for hydrogen upon the explosibility of methane

SUBSTANCE	FORMULA	EXPLOSIBILITY	LIMITS OF INFLAMMABILITY, PER CENT BY VOLUME	
			Lower	Upper
Methane	CH_4	Highly explosive with air	5 00	15 00
Methyl chloride	CH_3Cl	Moderately explosive with air	8 20	18.70
Methylene chloride	CH_2Cl_2	Not explosive with air	No explosive limits	
Chloroform	$CHCl_3$	Not explosive with air	No explosive limits	

cleaning compounds when added in the proper proportions to combustible liquids such as naphtha and petroleum distillates.

4. Elimination of ignition sources

Combustible gases and vapors, mixed with air or pure oxygen in the proportions to give explosive mixtures, may be safely used provided all sources of ignition are eliminated. Before a mixture can be made to explode, a portion of it must be heated to its ignition temperature. The ignition temperature may be defined as that temperature at which rapid combustion becomes independent of external supplies of heat.

It is not the purpose of this report to discuss ignition temperatures other than to state briefly that values reported in the literature are variable, can be used only in a relative sense, and may be even misleading unless complete details of the procedure by which the results were obtained are given. The results obtained depend upon and are affected by a number of variables, the most important of which are the percentage of combustible

in the mixture, the oxygen concentration, the "lag" or time required at a given temperature to cause ignition, the size, composition, and dimensions of the equipment in which the tests are made, the pressure at which the mixture is confined at the time of ignition, and the presence of catalysts and impurities in the mixtures.

The safety engineer is primarily interested in the sources of ignition that may cause explosions   These sources may be represented by the classification given below:

$$
\text{Ignition sources}
\begin{cases}
\text{Flames}
\begin{cases}
\text{Open lights} \\
\text{Matches and cigarette lighters} \\
\text{Fires in boilers; water heaters} \\
\text{Burning material; incinerators}
\end{cases} \\[2em]
\text{Sparks}
\begin{cases}
\text{Static electricity} \\
\text{Electrical shorts} \\
\text{Lightning} \\
\text{Sparks from tools}
\end{cases} \\[2em]
\text{Heated materials}
\begin{cases}
\text{Glowing metals, cinders, and filaments} \\
\text{Electric lights}
\end{cases}
\end{cases}
$$

Most of the sources of ignition given above can be taken care of by establishing proper safety regulations and installing flame-proof electrical equipment; others by designing the plants so that boilers, water heaters, and other equipment where there are open flames and incandescent materials are installed in other buildings at a safe distance from the place where the hazardous processes are carried out.

Static electricity has caused many serious fires and explosions and is one of the most serious ignition hazards to control.   There are few operations in which it may not be present, and it is more serious in dry atmospheres when the relative humidity is below 60 per cent.   Static is generated by friction, that is, by slipping belts, pulleys, and revolving machinery and by the passage of solids, liquids, or gases at high velocity through small openings.

Static electricity may be eliminated by grounding all machinery, pipes, and other equipment where charges may accumulate.   To accomplish this, permanent metallic conductors should be connected to the pipes of the water system.   In the case of moving equipment, metallic collectors or "combs" should contact the moving parts and so ground the charges that may collect on the equipment.

5. Segregation of hazardous operations

Operations which through necessity rather than choice require the use of inflammable gases or vapors should be segregated from other operations.

This requires the installation of hazardous processes in buildings at a safe distance from others and, if heavy combustible vapors are used, the elevation should be below that of other buildings so that in case of a fire or explosion the liquids and vapor that may be released will not flow toward other adjacent buildings. A hill or artificial earth barrier should be constructed where the operations are exceedingly dangerous.

6. The provision of adequate ventilation

The necessity for adequate ventilation in buildings cannot be too strongly emphasized where inflammable gases and vapors are handled and used. This includes not only the buildings in which the vapors are used but also all conduits, trenches, and tunnels where lines for conveying inflammable gases and vapors, and pipe lines for conveying inflammable liquids, are installed. Such lines should be carried in the open air above ground from one building to another, and in buildings they should be suspended above the floor level where they can be inspected readily for leaks.

Buildings should be made of light material which will offer not too great a resistance to pressure if an explosion occurs. The top should be provided with open ventilators, and windows should be installed in sashes of the tilting type which open when pressure is exerted from the inside.

It is impossible to have too much ventilation around hazardous operations. Where possible the operations should be carried out entirely in the open air, with no buildings whatever except those to house recording and other delicate instruments.

7. Construction of smooth fireproof floors

Smooth, fireproof floors resistant to the penetration of liquid combustibles should be used in buildings where hazardous operations are carried out. The floors should be laid directly on an earth foundation with no unventilated spaces underneath. They should be cleaned and scoured periodically. Many disastrous fires have been due to oils, greases, and hydrocarbon deposits being allowed to accumulate on the floors. Although such deposits are normally safe from explosion hazards, they may become exceedingly hazardous if a small fire or explosion develops in the plant, since because of the resulting high temperature the deposits vaporize and burn and are very difficult to extinguish when once set on fire.

8. Release diaphragm

Adequate light-weight release diaphragms should be provided on all equipment in which explosive mixtures may be present. The ideal release diaphragm is that having zero mass and an infinite area. This cannot be realized in practice; however, the construction and size of release openings

should approach the above ideal as closely as possible, yet be of sufficient strength to sustain the operating pressure within the equipment without danger of rupture or leakage except in the case of an explosion within the equipment.

To protect properly a given installation containing explosive mixtures, the following factors must be known or determined experimentally. (1) The type and concentration of explosive mixtures that may be present in the equipment. (2) The maximum pressure the equipment will safely stand. (3) The area of release openings necessary to keep the pressures below the safe maximum pressure. (4) The type of diaphragm material that will rupture at the desired pressures. (5) The location of the release diaphragms so that there will be no unprotected dead ends. Space does

TABLE 6

Pressures developed by explosive mixtures of acetone–air with varying sizes of release openings, in pounds per square inch above atmospheric pressure in 8-liter bomb

ACETONE, PER CENT BY VOLUME	ROUND HOLE, DIAMETER OF OPENING							SQUARE HOLE, WIDTH	
	Closed	0 25 in	0 50 in	1 00 in	2 00 in	3 00 in	4 00 in	1 5 in	2.5 in
3 00	36	17.0	7 0	2 0	0 5	0 5	0 5	0 5	0 5
4 00	61	40 0	20 0	7 0	2 5	0 5	0 5	2 5	0 5
5 00	74	65 0	45 0	12 0	4 0	1 5	0 5	5 0	1 5
5.50	78		49 0	14 0	4 5	2 0	0.5	6 0	2 0
Ratio = $\dfrac{\text{volume in cu. ft.}}{\text{area opening in sq. in}}$	Infinite	5 79	1.446	0 362	0 0905	0 0402	0 0226	0 126	0.0454
Area of opening in sq. in. per cu ft..	0 00	0.17	0 69	2 77	11 05	24 90	44 30	7 9	22 0

not permit a complete discussion of these factors, so only one example will be given to show how the proper diaphragm releases may be determined.

The pressures developed when mixtures of acetone and air of varying concentration are ignited in the bomb provided with different release openings are given in table 6. The results show that the maximum pressure developed in the bomb occurs when the concentration of acetone equals about 5.5 per cent by volume. Using the values giving the maximum pressure development for the various-size release openings tested, the curve shown in figure 5 is obtained. This gives the pressure developed when the area of release openings is varied from zero opening to 45 sq. in. per cubic foot of space in the equipment. Assume that the equipment should not be subjected to a pressure greater than 10 lb. per square inch, then

the area of release openings should be approximately 5 sq. in. per cubic foot of space

The next important factor is the determination of the proper size, material, and thickness of the diaphragm material which will provide release of the gases from the equipment at a pressure of 10 lb. or less.   In general, lead, tin, aluminum, or copper foil have been found to be most suitable for release material at low pressures.

One example will be shown of tests made on aluminum foil of 0.001 in. thickness in an 8-liter bomb when acetone-air mixtures were used for tests   The rupturing pressures for openings of different sizes and concen-
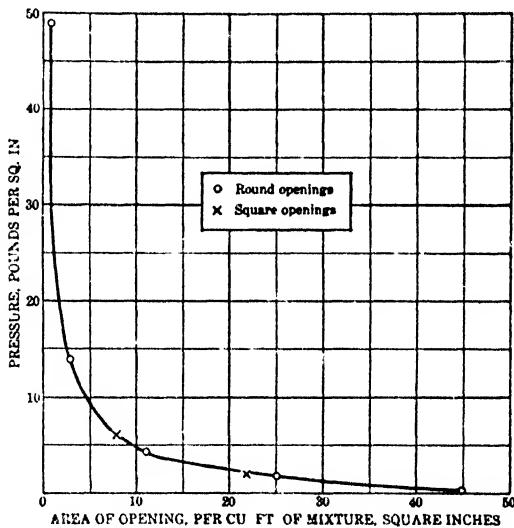
Fig 5. Curve of relation of pressures produced to area of opening, 5 50 per cent acetone-air mixtures   8 05-liter bomb.

tration of acetone in air are given in figure 6.   The rupturing pressure increases as the area of the opening is reduced.   In this example, where the pressure must not exceed 10 lb., the curves show that the diaphragms must be at least 3 in. in diameter if this aluminum foil is used, and the number of release openings should be such as to give 5 sq. in. of diaphragm opening per cubic foot of space in the equipment.

The pressure required to rupture a given diaphragm material is directly proportional to the ratio of the perimeter to the area.   This relation can be expressed by the equation

$$P = K\frac{S}{A}$$

in which P is the pressure required in pounds per square inch to rupture the diaphragm, A the area in square inches, S the perimeter in inches, and K a constant characteristic of the particular diaphragm material being used.

In practice, K is determined for any given diaphragm material by making tests of the material in an opening of any given size and determining the pressure developed when the diaphragm is ruptured. The determined value of K can then be used to calculate the rupturing pressure for openings of any size.

In addition to the above requirements demanded of release diaphragms to maintain the maximum developed pressure below a given safe pressure, the location and distribution of the release diaphragms are very important. Experiments made in round ducts 12 in. in diameter and 15 ft. in length with acetone and air mixtures showed that release diaphragms should be
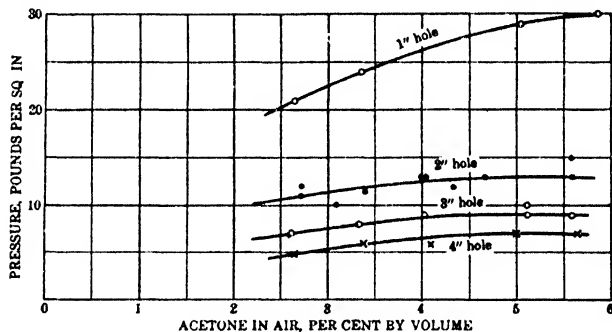
FIG. 6. Tests of aluminum diaphragms, 0 001 in. thick

distributed so that they were not more than 10 ft. apart, and that every dead end and sharp bend needed a diaphragm release to prevent the building up of pressure at these points.

9. Recorders for determining the concentration of combustibles in hazardous atmospheres

Combustible gas indicators or recorders should be installed in all equipment where hazardous concentrations of combustibles may be present, and sampling locations should be chosen so that samples may be taken from different locations. Equipment has been developed whereby samples may be taken periodically from twenty or more locations and recorded on one instrument.

It is not the purpose of this report to discuss the merits of indicators and recorders. There are recorders now marketed which operate on the thermal conductivity principle, others on the change in volume resulting

from the burning of the combustibles in the sample, while others depend upon the increase of resistance of a glowing filament when operating in an atmosphere containing combustibles; the greater the amount of combustibles present the greater the temperature of the wire and therefore the greater the resistance.

The performance and success of any of these devices can be determined only by actual installation in a representative plant and calibration of the device by chemical analysis against the particular combustibles used in the process.

REFERENCES

(1) BERL, E., AND BARTH, K · Z. Elektrochem. **39** 73 (1933).

(2) BURGESS, M J., AND GREENWOOD, G : U. S. Bur. Mines Bull. No. 279, pp. 71, 80, 81 (1931).

(3) BURGESS, M. J , AND WHEELER, R V : J. Chem Soc **99**, 2013–30 (1911)

(4) COWARD, H F , AND BRINSLEY, F : J. Chem. Soc **105**, 1859–85 (1914).

(5) COWARD, H F., CARPENTER, C., AND PAYMAN, W : J Chem. Soc **115**, 27 (1919).

(6) COWARD, H. F., AND JONES, G. W.: U S. Bur. Mines Bull. No. 279, 114 pp (1931).

(7) COWARD, H. F., AND JONES, G. W . Ind Eng Chem **22**, 963 (1930).

(8) COWARD, H. F., JONES, G W., DUNKLE, C G , AND HESS, B E.: Mining Met. Investigations, Carnegie Inst Tech , Bull. No 30, 42 pp (1926).

(9) FRANCK, H. H., AND DORING, G.: Angew Chem **44**, 273–7 (1931).

(10) HEMPEL, W : Gasanalytische Methoden Braunschweig (1913).

(11) JONES, G W.· U. S Bur Mines Tech Paper No 450, 38 pp (1929).

(12) JONES, G W.: Ind Eng Chem **20**, 367 (1928).

(13) JONES, G W., BAKER, E. S , AND MILLER, W E : From Annual Report of the Explosives Division, Fiscal Year 1936; U S Bur Mines Rept. Investigations No 3337, p. 17, February, 1937

(14) JONES, G. W., AND BEATTIE, B. B.: Ind Eng Chem **26**, 557–60 (1934).

(15) JONES, G. W., HARRIS, E. S., AND MILLER, W. E.: U S Bur. Mines Tech. Paper No 544, 26 pp. (1933).

(16) JONES, G. W., HARRIS, E S., AND BEATTIE, B B : U S. Bur. Mines Tech. Paper No. 553, 26 pp (1933).

(17) JONES, G. W., AND KENNEDY, R E : From Annual Report of the Explosives Division, Fiscal Year 1936; U. S. Bur. Mines Rept Investigations No. 3337, 17 pp., February, 1937.

(18) JONES, G. W., AND KENNEDY, R E : Ind Eng. Chem. **22**, 146 (1930)

(19) JONES, G W., AND KENNEDY, R E.: Ind. Eng Chem. **22**, 963 (1930).

(20) JONES, G. W., AND KENNEDY, R. E.: U′ S. Bur Mines Rept Investigations No. 3216, 24 pp., June, 1933.

(21) JONES, G. W., AND KLICK, J. R.: Ind Eng. Chem. **21**, 791 (1929).

(22) JONES, G W., AND MILLER, W E : U. S. Bureau of Mines Unpublished results.

(23) JONES, G. W., MILLER, W. E., AND SEAMAN, H : Ind. Eng. Chem. **25**, 694–6 (1933).

(24) JONES, G. W., SEAMAN, H., AND KENNEDY, R. E.: Ind Eng. Chem. **25**, 1283–6 (1933).

(25) JONES, G. W , MILLER, W. E., AND SEAMAN, H.: Ind Eng. Chem. **25**, 771 (1933).

(26) JONES, G W., YANT, W. P., MILLER, W. E., AND KENNEDY, R. E . U. S. Bur. Mines Rept. Investigations No. 3278, 5 pp., July, 1935.

26 G. W. JONES

(27) JONES, R. M.: Ind Eng. Chem. **25**, 394-6 (1933).

(28) LE CHATELIER, H., AND BOUDOUARD, O.· Compt. rend **126**, 1344, 1510 (1898).

(29) LE CHATELIER, H , AND BOUDOUARD, O : Bull soc chim **19**, 483 (1898).

(30) NAGAI, Y : Proc. Imp. Acad (Tokyo) **2**, 284-8 (1926).

(31) National Fire Protection Association, Committee on Flammable Liquids, Fire-Hazard Properties of Certain Flammable Liquids, Gases and Volatile Solids (1934)

(32) NUCKOLLS, A. H.: Method for the Classification of Hazardous Liquids   Underwriters' Laboratories, March, 1929, p. 6.

(33) RICHARDSON, E. G , AND SUTTON, G. R : Ind. Eng. Chem. **20**, 187 (1928).

(34) THORNTON, W M.: Phil Mag **33**, 190 (1917)

(35) WHEELER, R V.: U S Bur. Mines Bull. No 279, p 80 (1931)

(36) WHITE, A. G.: J Chem Soc. **125**, 2387 (1924)

(37) WHITE, A G.: J Chem. Soc **121**, 1244, 1688, 2561 (1922).

(38) WHITE, A. G : J Chem Soc. **115**, 1462 (1919)

(39) WHITE, A. G.: J. Chem. Soc **127**, 48 (1925)

(40) YEAW, J.: Ind Eng. Chem **21**, 1030 (1929)

A THERMODYNAMIC ANALYSIS OF THE RATE OF RISE OF PRESSURE IN THE OTTO CYCLE

GEORGE GRANGER BROWN

Department of Chemical and Metallurgical Engineering, University of Michigan, Ann Arbor, Michigan

Approximately two-thirds of the mechanical horsepower of the nation is developed by internal-combustion motors operating on the Otto cycle. In the ideal cycle (figure 2) the mixture is compressed adiabatically from 1 to 2, and the combustion is supposed to take place instantaneously at constant volume over the path 2-3. The burned gases then expand adiabatically from 3 to 4, at which point the exhaust valve opens and the mixture expands from 4 to 4', leaving within the cylinder that quantity represented by point 5. On the exhaust stroke from 5 to 6 most of the burned mixture is forced out of the engine cylinder, that volume represented by point 6 being retained in the clearance volume. The charge is then drawn in along the intake stroke from 6 to 1, and the cycle is repeated.

I. THE NORMAL CYCLE

The actual combustion does not take place instantaneously, but begins at a single point or zone where ignition occurs. Inflammation spreads rapidly throughout the entire mixture, with each succeeding part to be inflamed burning under conditions of higher pressure and temperature than the previous zone. Such a reaction is not a true homogeneous reaction in the sense that the gas is a single homogeneous phase during combustion, but only in the sense that the reaction takes place in a gas phase which is strictly a single phase only before and after combustion and is unaffected by surfaces Such a reaction has been called "progressive homogeneous" (2). The combustion may be expressed diagrammatically, as in figure 1. Condition A represents that immediately before ignition. B represents the complete inflammation of layer 1 and its expansion compressing the unburned gas ahead of the flame. Condition C represents the inflammation of layer 2, which expands and compresses the burned gases in layer 1 and the unburned gases ahead of the flame. The same procedure is indicated in a further stage of combustion in D.

If the combustion proceeds orderly in this manner at a moderately low

rate, pressure is equalized throughout the gaseous mixture as the flame advances. The normal combustion Otto cycle is an idealized cycle, assuming this type of normal combustion to take place while the piston is at top dead center. Figure 3 indicates the specific properties of the first and last layers of the mixture to burn in this manner as computed by the thermodynamic chart of Hershey, Eberhardt, and Hottel (13). The expansion and compression of the successive layers of gas burned in such a progressive combustion reaction establish a temperature gradient throughout the burned mixture, as may be computed (13) and as has been measured (14, 22).
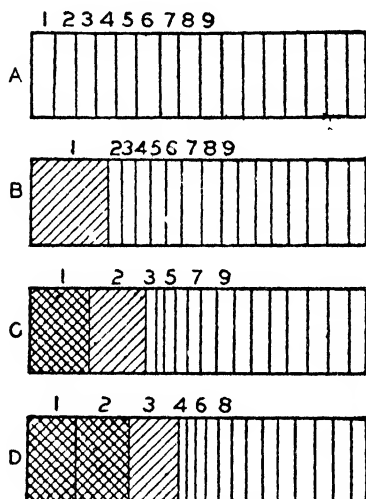
FIG. 1 Normal combustion. A represents the charge before ignition, B the conditions when layer 1 is inflamed, C the conditions when the flame has passed 1 and 2 is inflamed, and D the conditions with a fast burning mixture when pressure is not uniform but is concentrated in the flame front.

The use of the enthalpy–entropy charts takes into consideration changes in heat capacity and equilibrium in the product of combustion. They are considered to give reliable results depending upon the assumption made in their application. For convenience the computations that may be made by the use of the ideal gas equation, ignoring chemical equilibrium, have been outlined in the appendices.

The temperature gradient at the end of normal combustion, assuming adiabatic processes and no mixing, with uniform pressure distribution during combustion with the piston at top dead center, is computed as 1500°F for ideal gas mixture (see Appendix II(3)), and as 763°F. by means of the thermodynamic equilibrium chart. In each case a compres-

sion pressure of 160 lb. per square inch and a combustion pressure of 760 lb. per square inch absolute were assumed. The relatively large difference in the two methods is due to the fact that variations in heat capacity and dissociation have been accurately computed in the thermodynamic charts and neglected in the simple equations assuming ideal gases. An interesting comparison with experimental data is provided from tests on an engine of 4.4 compression ratio, using 80 per cent of theoretical air (22) in which a temperature gradient of about 600°F. was measured. The computed temperature gradient for this compression ratio, using 85 per cent of the theoretical air according to the thermodynamic chart (13), is 1030°F. When it is considered that 40° of crank revolution was required for com-
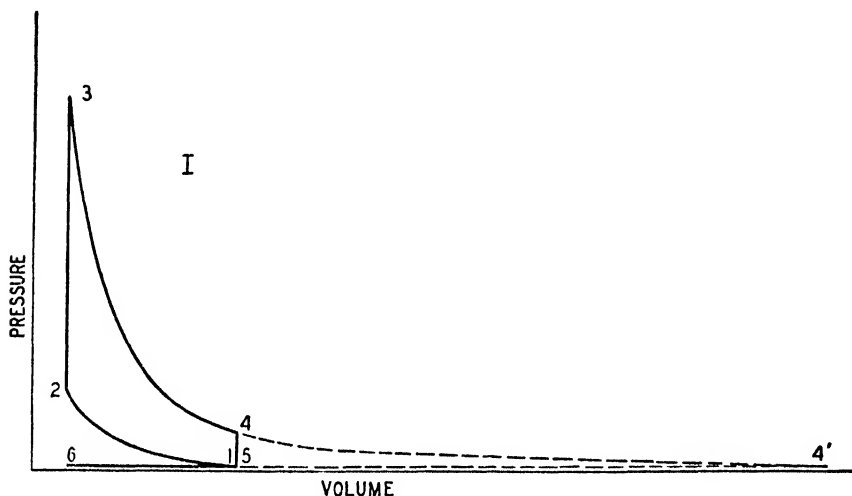
Fɪɢ. 2. Pressure–volume diagram of the ideal Otto cycle I

bustion in the engine, as well as that there were other differences, and that it is impossible to measure the temperature of the extreme first and last layers burned, the agreement appears satisfactory.

Insofar as efficiency and work are concerned, the ideal instantaneous combustion Otto cycle and the normal combustion Otto cycle are closely equivalent (13a). This is due to the fact that combustion occurs with the piston at top dead center in each case and with no important thermodynamic irreversibility other than that of the chemical reaction itself. These two cycles are identified as cycle I of figure 2 and cycle II of figure 3, as computed from the thermodynamic charts using 85 per cent of theoretical air (13). The properties of the working fluid at the various points as calculated are given in table 1. The slight differences between cycles I and
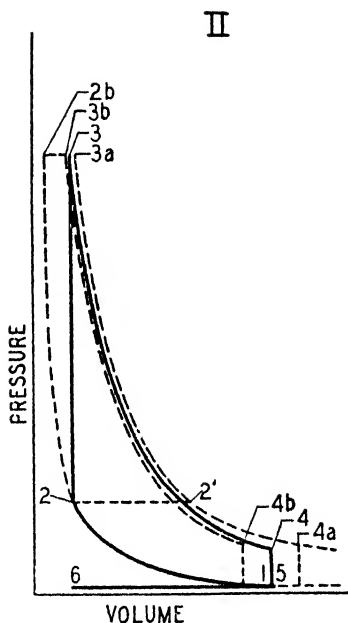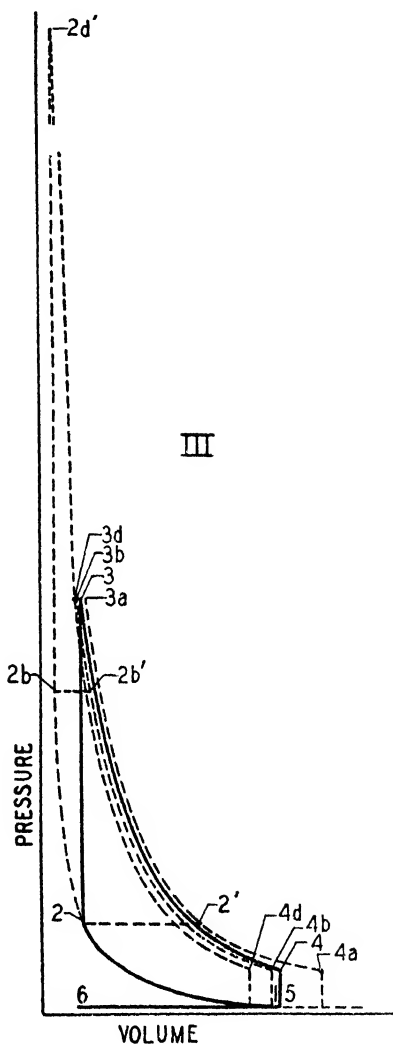
FIG. 3. Pressure–volume diagram of the normal Otto cycle. The solid lines represent average or effective properties, and the broken lines represent specific properties of the first (a) and last (b) parts of the mixture to be inflamed.

FIG. 4. Pressure–volume diagram of a knocking Otto cycle in which one-third of the charge detonates at constant volume. The solid lines represent average or effective properties and the broken lines specific properties of the first (a) and last (b) parts to burn normally with uniform pressure distribution and of the detonating (d) part of the mixture.

TABLE 1

Computed properties of working fluid in adiabatic Otto cycle

Compression ratio = 6

POINT	CYCLE	DESCRIPTION	ABSOLUTE TEMPERATURE R. T	ABSOLUTE PRESSURE LB PER SQ. IN. P	VOLUME OF GASES PER LB. OF AIR V	RELATIVE ENTHALPY PER LB. OF AIR H	RELATIVE INTERNAL ENERGY PER LB. OF AIR U	RELATIVE ENTROPY PER LB. OF AIR S
1	I, II, III	Begin compression	650	14 7	16.8		26,	
2	I, II, III	End of compression	1152	160	2 8		138,	0.11,
2$_b$	II	Last to burn at constant P	1640	760	About 0 9	1836		0.11,
2$_b$	III	Last to burn at constant P	1520	560	1 08	335,	228,	0.11,
3	I	End of combustion	4980	760	2 8		1585	0.576
2′	II, III	First to burn at constant P	4308	160	11 2	1676		0 633
2$'_b$	III	Last to burn at constant P	4600	560	3 55	1792		0.564
2$'_d$	III	Constant volume "detonating"	5255	2020	1.08		1675	0 520
		After equalization of P						
3$_a$	II	First to burn	5475	760	3.08		1840	0 633
3$_b$	II	Last layer to burn	4712	760	2.53	1836	1455	0.544
	II	Average 3$_a$ and 3$_b$	5093		2 8		1647	
3$_a$	III	First to burn	5430	725	3 25		1825	0 633
3$_b$	III	Last to burn at constant P	4825	725	2.56		1520	0 564
3$_d$	III	Constant volume "detonating"	4370	725	2.58		1350	0 52
	III	Average 3$_a$, 3$_b$, 3$_d$	4875		2 8		1565	
4	I	End of expansion	3300	80	16 8		1010	0.576
4$_a$	II	First to burn	3820	85	18 8		1180	0.633
4$_b$	II	Last to burn	3060	85	14 8		940	0 544
	III	Average 4$_a$ and 4$_b$	3440		16.8		1060	
4$_a$	III	First layer normal	3800	80	19.8		1160	0.633
4$_b$	III	Last layer normal	3200	80	16.2		980	0.564
4$_d$	III	Detonating	2835	80	14 7		870	0.52
	III	Average 4$_a$, 4$_b$, 4$_d$	3280		16.9		1003	
4′	I	End of exhaust		14.7	66	610	723	

II indicated in table 1 are due to the inexact but convenient use of arithmetical averages of the properties of the first and last layers of the mixture to burn. As the same procedure was used for the detonating cycle III as for the normal cycle II, these two cycles are comparable in all respects.

In these figures a solid line represents the average properties of the working fluid in the cycle. The dashed lines in figure 2 (cycle I) indicate the specific properties of the fluid at the end of expansion and with the exhaust valve open with the piston at lower dead center. The dashed lines in figure 2 (cycle II) indicate the specific properties of the first and last infinitesimal layers to be inflamed, assuming adiabatic conditions without mixing and uniform pressure distribution during combustion.

II. THE KNOCKING CYCLE

If the inflammation is accompanied by an extremely high rate of rise of pressure so that the pressure is not uniformly distributed throughout the mixture, as has been indicated in figure 1 D, which shows the layers 4 and 5 immediately ahead of the inflamed layer 3 compressed to a greater degree than the unburned gas toward the right end of the cylinder, a zone of high pressure is built up directly ahead of the flame and within the flame. Under these conditions the inflamed layers of gas at a high pressure expand very rapidly, compressing those layers of gas at low pressure in sequence with a velocity equal to the velocity of a sound wave in the gaseous medium (15). This action establishes a high intensity pressure wave traveling back and forth through the mixture and reflected from the walls of the combustion chamber. The immediate cause of such a pressure wave is the extremely high rate of rise of pressure developed in a part of the mixture and the extremely rapid expansion of this high pressure zone against the low pressure zone within the mixture. Such an expansion takes place with extreme speed and is thermodynamically highly irreversible, in that the work energy lost by the zone of high pressure equals

$$\int P_1 \mathrm{d}V$$

while the work done by the zone of high pressure on the zone of low pressure is equal to

$$\int P_2 \mathrm{d}V$$

Since $\mathrm{d}V$ is the same in the two expressions and P_1 is much greater than P_2 at the beginning of the expansion, although equivalent at the end, it is clear that the expansion of the high pressure zone against the low pressure zone is thermodynamically irreversible. However, the pressure immediately ahead of the high pressure zone is locally equal to P_1, because of the high velocity of expansion and the high rate of rise of pressure. Therefore

the path covered by the high pressure zone during expansion is correctly represented by an adiabatic path corresponding to the $\int P_1 dV$ above as is the $\int P_2 dV$ representative of the path for the low pressure zone.

The apparent loss in potential energy accompanying this irreversible expansion is evident in the high velocity intense pressure wave as kinetic energy, the conversion of potential energy into kinetic energy being necessary to accomplish the extremely rapid expansion caused by the high rate of rise of pressure in the high pressure zone.

In fuel–oxygen mixtures the rate of reaction and the rate of rise of pressure in the flame front are so intense that the condition outlined above is obtained in the case of an otherwise normal progressive combustion and results in the detonation wave (9, 26), in which the unburned mixture immediately ahead of the flame front is ignited and inflamed by the intense adiabatic compression, so that the detonation wave is supported by the inflammation which is part of the pressure wave itself.

In fuel–air mixtures the rate of reaction is retarded by the presence of diluent, and the true detonation wave is not ordinarily developed. However, in high-compression engines the compression of the unburned charge ahead of the flame front by the process of normal combustion in which the pressure is uniformly distributed in the manner described frequently brings the unburned charge to such a condition of temperature and pressure that it spontaneously bursts into flame, accompanied by an intensely high rate of rise of pressure due to the extremely rapid inflammation. The effect of this extremely high rate of rise of pressure caused by the autoignition, or "detonation", of the unburned charge results in the same type of spontaneous, thermodynamically irreversible expansion of the high pressure zone against the low pressure zone of gases in the combustion chamber immediately following such autoignition. This results in the intense pressure wave which is similar in most respects to the detonation wave described above, except that it is not accompanied by the simultaneous inflammation of an unburned mixture.

This mechanism of engine detonation has been indicated for many years on the basis of experiments in bombs (32, 7), and has been confirmed by photographic studies of detonating mixtures in the combustion chamber of an engine (25, 23). In these studies (23) normal combustion at 900 R.P.M. required 36° of crank rotation or about 0.0067 second for complete inflammation. Knocking or "detonating" combustion under the same speed and other conditions required a total of only 22° rotation or about 0.0041 second for complete inflammation. The normal combustion of approximately one-half by weight of the mixture required the same time in each case,—about 0.0036 second. But the autoignition of the last half of the charge in the knocking combustion required only about 0.0005 second for

complete inflammation.   The photographs (23) clearly indicate that auto-ignition and inflammation of the last half of the charge during 0.005 second takes place without observable change in the position of the previously burned gases, that is, at substantially constant volume.

In figure 4 is shown cycle III, which represents the normal combustion of two-thirds of the explosive mixture followed by autoignition or detonation of the last third of the mixture, computed by means of the thermodynamic charts (13), assuming 85 per cent of theoretical air and the same compression ratios and initial conditions as for cycles I and II.   The normal combustion of the first two-thirds of the mixture was assumed to take place with uniform pressure distribution throughout the charge, and the autoignition or knocking of the last third of the mixture to be inflamed was assumed to take place at constant volume.   The entire process is assumed to be adiabatic, and the various zones of gases are assumed to expand or to be compressed without mixing under adiabatic conditions in the same manner as was assumed in computing the normal combustion of cycle II (13) represented in figure 3.

The properties of the working fluid corresponding to the different points in cycle III are included in table 1.   It will be noted that the compression of the charge along the path 1-2 is the same for all three cycles.   The first infinitesimal layer to be inflamed is ignited under conditions corresponding to point 2 and burned with pressure constant and uniformly distributed throughout the mixture along the path 2-2'.   Along this path the enthalpy of the mixture remains constant.   Normal combustion proceeds in successive layers compressing the unburned mixture ahead of the flame adiabatically along the path 2-2b.   At 2b the last layer is inflamed and burns at constant pressure 2b-3b.   In cycle II this completes the entire combustion.   But in the knocking cycle III this normal combustion is assumed to continue for only two-thirds of the charge, and upon combustion of the last layer to burn normally along the path 2b-2b', one-third of the charge, at conditions corresponding to 2b, is still uninflamed.

In cycle III the balance of the combustion is assumed to take place at constant volume along the path 2b to 2d'.   At the instant of the completion of this constant volume combustion or autoignition of the last third of the charge, that part of the charge which has burned normally is at the pressure represented by the horizontal line 2b-2b', while that part which has detonated is at the pressure 2d'.   This large difference in pressure requires that the high pressure zone at the pressure 2d' expand with a high velocity along the adiabatic path 2d'-3d, thereby compressing the previously burned charge for the pressure 2b' to the point 3b for the last layer to be burned normally and to the point 3a for the first layer to be burned.   After this expansion the mean effective pressure corresponds to point 3.

This is the pressure which is effective on the piston in doing useful work, as the instantaneous high and low pressures in the high velocity pressure wave are not effective in accomplishing any useful work on the piston.

The computation for this adiabatic irreversible expansion has been made in exactly the same way as was proposed by the authors of the charts (13) for handling the irreversible expansion of the exhaust gases from the combustion chamber through the exhaust valve to atmospheric pressure at the end of the expansion zone.   The temperatures and pressures of the various parts of the mixture so computed and listed as table 1 indicate that the maximum temperature in the detonating combustion is found not in that part of the mixture to detonate (point 2d, cycle III) but in the first layer of mixture to be inflamed (point 3a, cycle III).   This difference in temperature persists throughout the expansion stroke in the same manner as the temperature gradient in normal combustion cycle II previously discussed.

The pressure developed in the detonating part of the charge is much higher than that effective in any other part of the mixture.   In table 1 an absolute pressure of 2020 lb. per square inch is indicated for the detonating part of the charge, as compared with an effective pressure of 725 lb. per square inch absolute for other parts of the charge.   It is true that this high pressure in the detonating charge exists only for an extremely short interval of time and that it is not effective in doing work on the piston, although it has been referred to as an effective pressure because it is the motivating force for the high pressure wave which is set up in detonating explosions (25) and is accompanied by enormous acceleration in the pressure-time curve of the detonating portion of the charge.

If the observed time of autoignition at 900 R.P.M. for one-half of the charge (23) be assumed as the time interval for the detonation of one-third of the charge in cycle III, the average rate of rise of pressure during the detonation would be

$$\frac{2020 - 560}{0.0005} \text{ or } 2{,}920{,}000 \text{ p.s.i. per second}$$

The average rate of rise of pressure for the normal combustion preceding knock may be estimated as

$$\frac{560 - 160}{0.0036} \text{ or } 120{,}000 \text{ p.s.i. per second}$$

These figures indicate an average acceleration of the rate of rise of pressure during detonation or knock of about

$$\frac{2{,}920{,}000 - 120{,}000}{0.0005} \text{ or } 5{,}600{,}000{,}000 \text{ p.s.i. per second per second}$$

Maximum acceleration of the pressure–time curve during detonation at speeds of 2000 R P.M. might be 10 to 500 times this estimated average. Such forces exerted on the head and piston of the engine cause an accelerated deflection of engine parts, resulting in a maximum deflection greater than would be caused by the application of the same maximum pressure if the maximum pressure had been attained more gradually (16).

These enormous forces developed by the detonating part of the charge have an intense local action on the surrounding part of the combustion chamber and may be the true cause for the destruction of part of alloyed pistons when operated under severe detonating conditions. The apparent fusion of such pistons in the detonating zone cannot be due to the temperature developed therein, as this is actually less than that developed in the first layer to burn (compare point 2d and point 3a of cycle III in table 1).

The computed average effective pressure at the end of combustion for cycle III is 725 lb. per square inch, as compared with 760 lb. per square

TABLE 2

Computed effect of knocking on power and efficiency in adiabatic Otto cycle

Compression ratio = 6

	NORMAL	KNOCKING
Cycle	II	III
Work done = $(U_3 - U_4) - (U_2 - U_1)$ averages, in B t. u	475	450
Calculated efficiency based on $19,240 \times 0.0749$ B t u for net heat combustion of fuel per pound of air, in per cent	32 9	31 0
Mean effective pressure, in pounds per square inch	182	172

inch for the normal cycle II. This loss in effective pressure chargeable to the thermodynamic irreversibilities involved in the mass equalization of pressure following combustion results in a loss of about 5.5 per cent in net work, efficiency, and mean effective pressure of the cycle, as indicated in table 2.

The application of the ideal gas laws to the computation of such a knocking cycle (11) is indicated in Appendix II(4), with an indicated average pressure for the end of combustion (point 3) of 730 lb. per square inch as compared with 725 lb. per square inch for cycle III computed from the charts (13)

Since the power developed by such cycles depends entirely upon the increase in pressure accompanying combustion, it is interesting to note that the loss in work and efficiency due to knocking is proportional to the loss in effective rise in pressure upon combustion. This loss in rise of pressure is computed as 5 per cent, using the ideal gas equation as in

Appendix II, and 5.83 per cent as computed by the thermodynamic charts (13).

An experimental confirmation of the loss in power due to detonation as computed upon these assumptions is provided by test data taken on a variable compression N.A.C.A. Universal test engine and reported some
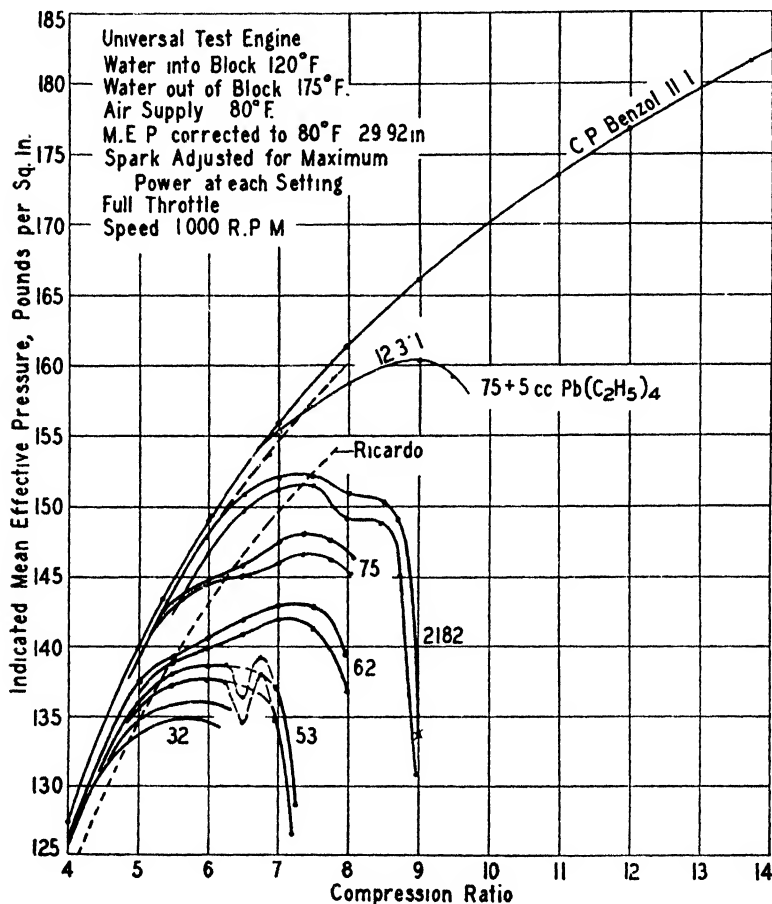
FIG. 5. The effect of compression ratio on the power (mean effective pressure) developed by different fuels in the N.A C A Universal test engine.

years ago (3). Figure 5, reproduced herein, is a plot of the mean effective pressure as a function of compression ratio as observed for different fuels. Fuel 2182 developed incipient detonation at a compression ratio of about 6.

The increase in compression ratio beyond that at which incipient detona-

tion develops, sufficient to cause detonation of one-third of the mixture as assumed for cycle III, may be computed by equation 17 as derived in Appendix I(4), as has been done in Appendix II(4). As indicated therein, an increase in compression ratio of about 33 per cent based on a compression ratio of 6.25 for incipient detonation, would be sufficient to cause the last third of the charge to detonate.

At a compression ratio of 8, which is an increase of 33 per cent over a compression ratio of 6, fuel 2182 developed a mean effective pressure of about 151 lb. per square inch, compared with a mean effective pressure of about 161 lb. per square inch for benzene, which does not detonate under these conditions. The mean effective pressure developed by benzene is about 1 per cent greater than that developed by fuel 2182 at lower compression ratios where neither fuel knocked. Making this adjustment for the different fuels, as indicated by the dashed extension of the curve for fuel 2182 in figure 5, the loss in mean effective pressure caused by detonation of fuel 2182 at a compression ratio of 8 is about 9 lb., as compared with a mean effective pressure of 160 lb. for non-detonating conditions. This corresponds to a loss of 5.6 per cent for the computed detonation of one-third of the charge. This is in excellent agreement with the 5.5 per cent computed for an idealized cycle by the thermodynamic charts (13) as given in table 2.

Similar calculations for fuel 62, which showed incipient detonation at a compression ratio of 4.7, indicates a loss in mean effective pressure of 5.3 per cent due to detonation at a compression ratio of 6.3, which is an increase of 33 per cent over that compression ratio required for incipient knock. Similarly fuel 75, showing incipient detonation at a compression ratio of about 5.3, indicates a loss in mean effective pressure of 5.1 per cent, owing to detonation at a compression ratio of 7.1.

These test results on different fuels of different knock ratings, showing approximately the same relative loss in mean effective pressure on detonation as computations based on adiabatic cycles, indicate that the loss in power and efficiency due to detonation may have a thermodynamic explanation in the loss of availability in the thermodynamic irreversibility of pressure equalization after detonation independent of any increased loss of heat by heat transfer from the gases to the jacket. The conversion of heat into work is a "second law" problem and is greatly reduced by thermodynamic irreversibility.

If the kinetic energy evident in the intense pressure wave caused by detonation were immediately converted to heat energy by absorption within the gaseous mixture, it might be expected that there would be no loss in power to the detonation. But the photographs of detonating combustion in engines show that these pressure waves persist for some

time (25), and it would appear more reasonable to assume that they are damped by the absorption of their energy in the walls of the combustion chamber rather than by the mixture itself. The computation based on an adiabatic cycle confirms this interpretation. As correctly stated by Rassweiler and Withrow (24), this loss in power and efficiency "must be accounted for by differences between knocking and non-knocking explosions other than a temperature difference of the gases", as they had observed that the temperature of the gases was actually lower in knocking combustion than in normal combustion. This difference is also evident in the computed cycles III and II as indicated in table 1. Increased heat transfer due to the pressure waves following detonation may be an unnecessary assumption.

These pressure waves of high intensity developed by detonation must not be confused with the vibrations which are frequently observed in normal burning mixtures (9, 15) even if such vibrations take on the properties of a pressure wave (26), owing to the acceleration of the flame (9) and the accompanying intensification of the vibrations as it passes through the flame front. These vibrations are apparently caused by oscillations in the igniting spark (26); when suppressed or eliminated by proper control of the spark no shock wave was developed upon autoignition in a cylindrical bomb (26).

These pressure waves, combined with a high rate of rise of pressure in the last part of the mixture to burn, may be the cause of roughness in engines, as in bomb experiments this combination was found to develop sound and vibrations in a similar manner (26).

III. ROUGHNESS

Intermediate in outward characteristics to knocking and normal combustion is another phenomenon characterized as "roughness", which is caused by high rates of rise of pressure or, more correctly, by high accelerations in the rate of rise of pressure. Janeway (16, 17) has analyzed combustion as related to roughness and has set forth the quantitative characteristics of two normal explosions (table 3), each developing the same maximum pressure with uniform pressure distribution throughout the combustion period, but one of smooth combustion characteristics and the other rough.

If the combustion chamber and location of the spark plug are so designed that the increase in volume of the flame with length of travel from the source of ignition is large during the early part of combustion and reduced during the later stages of combustion, the rate of rise of pressure is more nearly uniform with greatly reduced maximum acceleration (16, 17). This makes for a smooth combustion and a retarded rate of rise of pressure

during the combustion of the last part of the charge. This design is equivalent to igniting the mixture in a conical chamber by placing the spark plug centrally a short distance in from the base. The larger volume of the charge is then inflamed before it has been highly compressed by the expansion of previously inflamed mixture, and a much smaller part is burned under conditions which tend toward a high rate of rise of pressure. This tends to increase the acceleration in the rate of rise of pressure during the early part of combustion and to reduce the high acceleration which would otherwise occur in the last part of the mixture to be inflamed. The result is a smooth combustion which is otherwise difficult to obtain in high-compression motors.

TABLE 3

Quantitative comparison of smooth and rough engine (17)

	SMOOTH	ROUGH	RELA-TIVE
Maximum rate of rise			
Pressure, in pounds per square inch per second	162,300	34,000	2.18
Restoring force, in pounds per square inch per second	188,370	465,000	2.47
Maximum acceleration in rise			
Pressure, in pounds per square inch per second per second	93,000,000	567,000,000	6 1
Restoring force, in pounds per square inch per second per second	149,000,000	605,000,000	4.05
Relative kinetic energy of deflecting mass, $(2 47)^2$			6 10
Maximum restoring force, in pounds per square inch	439	543 7	
Maximum pressure, in pounds per square inch	410	410	
Shock factor,* per cent	7 07	32.6	4 6

$$*\left(\frac{\text{Maximum restoring force} - \text{maximum pressure}}{\text{Maximum pressure}} - 1\right)$$

Roughness may result from a high acceleration of the rate of rise of pressure from any cause, and should not be considered simply a mild form of detonation, which apparently always involves autoignition. The cause of roughness may be a distortion of the engine parts (16, 17), similar to but much less severe than that accompanying detonation, which sets up a vibration, or it may be caused by a transverse vibration of the crankcase which passes through a cycle in the same time as the periodic force which produces it, thereby increasing in amplitude from cycle to cycle until the damping forces become equal to the exciting force (12).

IV. THE RATE OF RISE OF PRESSURE

In order to control roughness, it has been found necessary to limit the maximum acceleration in the time rate of rise of pressure of the combustion. The rate of rise of pressure in the combustion is also a major factor in the control of detonation.

Combustion in the engine (23, 24) is, in all respects so far investigated, similar to the combustion of gaseous mixtures in bombs of constant volume (15, 26). The high degree of turbulence present in high speed engines and absent in bombs serves to increase greatly the speed of inflammation in normal combustion without appreciable change in the mechanism of combustion. This indicates that the reaction is heterogeneous in nature, that is, involving gases in more than one phase at one instant, and that the mechanism of the spread of flame through the mixture involves the transfer of heat or of material substance from inflamed gases to uninflamed gases ahead of the flame.

The results of computations based on the ideal gas laws are qualitatively correct in analyzing the Otto cycle and may also be used to indicate the effect of some factors controlling the rate of rise of pressure during combustion. By this procedure (4), which is briefly summarized in Appendix I(5), it may be shown (equation 20) that the rate of rise of pressure varies directly as some power of the pressure at which the gas is ignited.

The effect of temperature is more complicated but it has been shown (4, 21) that there is a real positive critical initial temperature at which the explosion develops its maximum rate of rise of pressure. This is true whether this critical initial temperature is determined under conditions of constant initial pressure, as is the case when the temperature of the mixture in the intake manifold is varied at constant throttle and speed, or under conditions of constant density, as is the case when the mixture temperature is varied after a positive displacement supercharger or after being confined within the cylinder. But the critical temperature is not the same under these different conditions (21).

V. FUEL CHARACTERISTICS

Autoignition develops a very high rate of rise of pressure with loss of available work energy and is by its nature a different reaction from normal combustion. It has been indicated (7) that the tendency of a fuel to knock in an engine may be estimated as varying directly with its rate of rise of pressure upon normal combustion and inversely with its ignition temperature. The rate of rise of pressure is directly proportional to the rate of reaction, which is also related to the "ignition lag" (28), so that perhaps all of us are really talking about the same thing but using different language. In any case, it appears that both factors must be considered in

autoignition, although only the rate of reaction need be considered in the case of normal combustion and the detonation wave.

In actual engine operation it is frequently observed that cracked petroleum fuels of an unsaturated and aromatic character are apparently depreciated in antiknock quality as compared with that which would be expected from laboratory tests. It has also been observed that supercharged engines do not so depreciate these fuels. It has been shown (21) that a supercharged engine is operating above the critical initial temperature for maximum rate of rise of pressure, while the normal engine is usually operating below. If the knocking tendency of a fuel is a function of autoignition temperature and rate of rise of pressure (or reaction), the knocking tendency would be increased more noticeably by an increase in temperature in the normal engine, which is below the critical initial temperature, than by an increase in temperature in the supercharged engine, which would tend to decrease the rate of rise of pressure and thereby tend to compensate for the other effects of temperature in stimulating autoignition. These observations would be particularly applicable to aromatic fuels, because of their high autoignition temperature (19).

In at least one case (10) it was found that engine detonation could be eliminated by increasing the inlet temperature when operating at high temperatures, which would be expected if the operation were conducted at a temperature above the critical initial temperature and with a fuel of high autoignition temperature.

VI. SUMMARY

The thermodynamic approach to combustion and the rate of rise of pressure in the Otto cycle are fruitful in analyzing the effect of different conditions upon the operation of the cycle. It is suggested that the thermodynamic method is an important tool in explaining and analyzing known characteristics such as "engine knock", roughness, and the effect of supercharging on the relative knock ratings of different types of fuels, and also a means of predicting characteristics of such combustion cycles as in the case of the critical initial temperature giving maximum rate of rise of pressure.

REFERENCES

(1) BEATTY AND EDGAR: J. Am. Chem. Soc. **56**, 102, 107 (1934).
(2) BROWN, G. G.: Ind. Eng. Chem. **17**, 1229 (1925).
(3) BROWN, G. G.: Oil Gas J. **27**, 156 (1929).
(4) BROWN, LESLIE, AND HUNN: Ind. Eng. Chem. **17**, 397 (1925).
(5) BROWN AND WATKINS: Ind. Eng. Chem. **19**, 280 (1927).
(6) BROWN AND WATKINS: Ind. Eng. Chem. **19**, 363 (1927).
(7) BROWN AND WATKINS: Ind. Eng. Chem. **19**, 366 (1927).
(8) CARR AND BROWN: Ind. Eng. Chem. **21**, 1071 (1929).

(9) DIXON: Trans. Roy. Soc. (London) **A200**, 319 (1903); S. A. E. Journal **9**, 237 (1921)

(10) DUMANOIS, P.: Ann. combustibles liquides, **9**, 143 (1934).

(11) GOOD, C. W.: Unpublished discussion (Society of Automotive Engineers, 1936) and private communication.

(12) HELDT, P M.: S.A.E. Journal **38**, 47 (1936).

(13) HERSHEY, EBERHARDT AND HOTTEL: S A E. Journal **39**, No. 4, 409 (1936).

(13a) HOTTEL AND EBERHARDT: Chem. Rev. **21**, 439 (1937).

(14) HOPKINSON: Proc. Roy. Soc. (London) **77**, 387 (1906).

(15) HUNN AND BROWN: Ind. Eng. Chem. **20**, 1032 (1928).

(16) JANEWAY, R. N . S.A E. Journal **24**, 92 (1929).

(17) JANEWAY, R. N : S.A.E Journal **24**, 139 (1929)

(18) LEWIS, B : S A E. Journal **36**, 134 (1935)

(19) MOORE: Automobile Eng **10**, 199 (1920)
TIZARD AND PYE: Phil Mag **44**, 79 (1922).
ORMANDY: J. Inst Petroleum Tech. **10**, 335 (1924)

(20) PEASE, R. N : J. Am. Chem Soc. **51**, 1839 (1929).

(21) PEARL AND BROWN: Ind. Eng. Chem. **28**, 1058 (1936).

(22) RASSWEILER AND WITHROW: S A.E. Journal **36**, 125 (1935).

(23) RASSWEILER AND WITHROW: S.A.E Journal **39**, 297 (1936)

(24) RASSWEILER AND WITHROW: Ind. Eng. Chem **28**, 672 (1936)

(25) RASSWEILER AND WITHROW: Ind Eng. Chem. **24**, 528 (1932).

(26) SOUDERS AND BROWN: Ind. Eng. Chem. **21**, 1261 (1929).

(27) VAN COVERN, F : Am Petroleum Inst Quarterly **7**, No 2, 6 (1937).

(28) VON ELBE AND LEWIS: Ind Eng Chem **29**, 551 (1937).

(29) WITHROW AND RASSWEILER: Ind Eng. Chem **25**, 923 (1933)

(30) WITHROW AND RASSWEILER: Ind Eng Chem. **25**, 1359 (1933)

(31) WITHROW AND RASSWEILER: Ind Eng Chem. **26**, 1256 (1934).

(32) WOODBURY, LEWIS AND CANBY: S.A.E. Journal **8**, 209 (1921).

APPENDIX I

1. THE INCREASE IN PRESSURE ON COMBUSTION

Assume an ideal gas with constant specific heats to which heat is added equivalent to combustion

V_A = the constant volume of the combustion chamber,

V_1 = the volume of a portion of the mixture before combustion,

V_2 = the volume of this portion after combustion,

Q = the heat liberated by combustion of unit volume of mixture,

QV_1 = the quantity of heat available to V_1 liberated by combustion of V_1,

$$QV_1 = \Delta U_1 + W \tag{1}$$

ΔU_1 = the increase in energy content of the portion of mixture burned, evident in increased temperature,

W = the work done by V_1 on $V_A - V_1$ due to expansion of V_1 to V_2,

$$\Delta U_1 = \frac{P_2 V_2 - P_1 V_1}{K - 1} = (T_2 - T_1) C_v \tag{2}$$

$$W = \frac{P_2(V_A - V_2) - P_1(V_A - V_1)}{K - 1} \tag{3}$$

$K = C_p/C_v =$ ratio of specific heat at constant pressure to that at constant volume,

$$QV_1 = \frac{(P_2 - P_1)V_A}{K - 1} = \frac{V_A \Delta P}{K - 1} = \frac{V_A \Delta P C_v}{R} = \frac{T_A \Delta P C_v}{P_A} \qquad (4)$$

$$\Delta P = \frac{QV_1 P_A}{C_v T_A} = \frac{QV_1 R}{C_v V_a} = \frac{QV_1 Rr}{C_v V_0} \qquad (4a)$$

where $r =$ the compression ratio $\dfrac{V_A}{V_0}$ and $V_0 =$ the volume of the charge prior to compression.

The increase in pressure (ΔP) is directly proportional to the portion burned (V_1) and the initial pressure (P_A) and inversely proportional to the heat capacity (C_i) and the original or initial temperature (T_A). For constant intake conditions (V_0), the increase in pressure (ΔP) upon combustion varies directly as the fraction burned and the compression ratio (r) and inversely as the heat capacity (C_v)

2 THE SPECIFIC VOLUME OF A SMALL UNIT MASS OF THE CHARGE (AS REPRESENTED BY AN INDIVIDUAL LAYER IN FIGURE 1) IN NORMAL COMBUSTION

Considering the combustion of successive infinitesimal layers with uniform pressure distribution as in normal combustion,

$V_0 =$ the original volume of small unit mass of the charge,

$V_c =$ the volume of such mass after being compressed adiabatically by the burning of other portions, and at which it is inflamed,

$V_e =$ the volume to which such mass expands at constant pressure during inflammation and combustion, and

$V_f =$ the final volume of such mass after further adiabatic compression by the burning of succeeding portions, the whole at P_f.

In the first step of adiabatic compression of unburned gas by previous combustion of other parts

$$V_c = \left(\frac{P_0}{P_c}\right)^{\frac{1}{K}} V_0 \qquad (5)$$

In the second step of combustion at constant pressure

$$QV_0 = C_p(T_2 - T_1) = \frac{P_c(V_e - V_c)K}{K - 1} \qquad (6a)$$

From which

$$V_e = \frac{Q(K - 1)V_0}{KP_c} + V_c \qquad (6)$$

In the third step of adiabatic compression of the burned gas by later combustion of other parts

$$V_f = \left(\frac{P_c}{P_f}\right)^{\frac{1}{K}} V_e \qquad (7)$$

Substituting equation 5 in equation 6 and the result in equation 7 and rearranging

$$V_f = \frac{(P_c)^{\frac{1}{K}-1} Q(K - 1)V_0}{(P_f)^{\frac{1}{K}} K} + \left(\frac{P_0}{P_f}\right)^{\frac{1}{K}} (V_0) \qquad (8)$$

3. THE PRESSURE DEVELOPED IN THE MIXTURE ACCOMPANYING DETONATION

If combustion of any part takes place with extreme speed so that pressure is not distributed, that portion so burning or "detonating" may be assumed to burn under conditions of constant volume. P_d = the pressure developed by "detonation" of that part of the charge burning at constant volume.

From equation 4, remembering that V_c now equals total volume to burn at constant volume and that all of this volume does so burn ($V_1 = V_A$)

$$QV_0 = \frac{(P_d - P_c)V_c}{K-1} \quad \text{and} \quad Q = \frac{P_f - P_0}{K-1}\frac{V_0}{V_0}$$

$$P_d = \left(\frac{Q(K-1)V_0}{V_c}\right) + P_c = \left(\frac{(P_f - P_0)V_0}{V_c}\right) + P_c \tag{9}$$

$$T_d = \left(\frac{P_d}{P_c}\right)T_c = \frac{(P_f - P_0)V_0 T_c}{P_c V_c} + T_c \tag{10}$$

Consider that part of the charge burns normally with pressure uniformly distributed, followed by constant volume combustion without uniform pressure distribution, that is, "detonation" of the last part, and that the pressure is equalized after combustion, rather than during combustion, by adiabatic compression and expansion.

P_x = final pressure after equalization after "detonation,"

V_x = final volume of unit mass after such combustion,

V_{xn} = final volume of unit mass that burns normally,

V_{xd} = final volume of unit mass that "detonates," and

P_f = final pressure resulting from normal combustion as before.

Since the total volume of the entire charge remains constant

$$\sum V_{xn} + \sum V_{xd} = \sum V_0$$

Since the quantity burned in normal combustion is proportional to the increase in pressure (equation 4),

$$\sum_{P_0}^{P_c} V_{xn} + V_{xd}(P_f - P_c) = V_0(P_f - P_0) \tag{11}$$

From equation 8

$$\sum_{P_0}^{P_c} V_{xn} = \int_{P_0}^{P_c}\left[P^{\frac{1-K}{K}}\frac{(P_f - P_0)V_0}{K(P_x)^{\frac{1}{K}}} + \left(\frac{P_0}{P_x}\right)^{\frac{1}{K}}V_0\right]dP$$

$$= \frac{(P_f - P_0)V_0\left(P_c^{\frac{1}{K}} - P_0^{\frac{1}{K}}\right)}{P_x^{\frac{1}{K}}} + \left(\frac{P_0}{P_x}\right)^{\frac{1}{K}}V_0(P_c - P_0) \tag{12}$$

$$V_{xd} = \left(\frac{P_d}{P_x}\right)^{\frac{1}{K}}V_c \qquad V_c = \left(\frac{P_0}{P_c}\right)^{\frac{1}{K}}V_0$$

and equation 9 gives

$$V_{xd} = \left[\frac{(P_f - P_0)\left(\frac{P_c}{P_0}\right)^{\frac{1}{K}} + P_c}{P_x}\right]^{\frac{1}{K}} \left(\frac{P_0}{P_c}\right)^{\frac{1}{K}} V_0$$

$$= \left[(P_f - P_0)\left(\frac{P_0}{P_c}\right)^{1-\frac{1}{K}} + P_0\right]^{\frac{1}{K}} \left(\frac{1}{P_x}\right)^{\frac{1}{K}} V_0 \tag{13}$$

Substituting equations 12 and 13 in equation 11, cancelling V_0, and solving for

$$P_x^{\frac{1}{K}} = P_c^{\frac{1}{K}} - \frac{\left\{P_0^{\frac{1}{K}} - \left[(P_f - P_0)\left(\frac{P_0}{P_c}\right)^{1-\frac{1}{K}} + P_0\right]^{\frac{1}{K}}\right\}(P_f - P_c)}{P_f - P_0} \tag{14}$$

$$P_x^{\frac{1}{K}} = \left[\left(\frac{P_c}{P_0}\right)^{\frac{1}{K}} - \frac{1 - \left[\left(\frac{P_f}{P_0} - 1\right)\left(\frac{P_0}{P_c}\right)^{\frac{K-1}{K}} + 1\right]^{\frac{1}{K}}}{\frac{P_f}{P_0} - 1}\left(\frac{P_f}{P_0}\frac{P_c}{P_0}\right)\right] P_0^{\frac{1}{K}} \tag{14a}$$

4. THE EFFECT OF COMPRESSION RATIO ON THE QUANTITY OF CHARGE DETONATING

If an engine is operated at such compression ratio as to be at the limit of normal combustion, that is, so that any higher compression would result in incipient detonation, the compression ratio at which any degree of knock will occur or the degree of knock for any other compression ratio may be estimated by the following equations: From equation 4a

$$\Delta P = \frac{xRr}{C_v V_0}$$

where x = the fractional part of charge burned and r = compression ratio $\frac{V_0}{V_A}$.

The pressure reached on completion of normal combustion of x part of the mixture

$$P_a + \Delta P = P_0(r)^K + \frac{xRr}{C_v V_0} \tag{15}$$

For the same intake conditions with the same mixture to obtain the same pressure at end of normal combustion

$$P_0(r_1)^K + \frac{x_1 R r_1}{C_v V_0} = P_c(r_2)^K + \frac{x_2 R r_2}{C_v V_0} \tag{16}$$

For the same pressure of combustion of the last layer to burn normally

$$P_b = P_0(r_2)^K + \frac{\Delta P}{r_1}(x_2 r_2) \tag{17}$$

where P_b = absolute pressure of the last part to burn normally and P_0 = absolute intake pressure.

If chemical equilibrium be assumed for the products of combustion, similar calculations may be made by use of the thermodynamic charts (13), without assuming ideal gases. In computing the effects of detonation as indicated by these equations, the results are similar by both methods.

5. THE RATE OF RISE OF PRESSURE ON COMBUSTION AS INFLUENCED BY CONDITIONS AND PROPERTIES OF THE MIXTURE

Considering the ideal combustion at constant volume and writing equation 4 in the differential form, and dividing by "dt", the time rate of rise of pressure $\left(\dfrac{dP}{dt}\right)$,

$$\frac{dP}{dt} = \frac{P}{TC_v}\left(\frac{dQ}{dt}\right) = \frac{Phk}{TC_v} \tag{18}$$

where C_v = heat capacity of products of combustion per unit of mixture,

$\quad t$ = time,

$\quad h$ = heat of combustion per unit of mixture, and

$\quad k$ = specific reaction velocity and number of units reacting per unit of mixture per unit of time

It has been shown (4) that, even in this ideal homogeneous reaction, k has a maximum value for any particular pressure at some finite positive temperature when the order of the reaction is greater than 1. This was demonstrated theoretically on the basis of the well-known effects of temperature and density upon the velocity of gaseous reaction, which lead to the following equation:

$$k = C\left(\frac{P}{T}\right)^{a-1}(e)^{-\frac{B}{T}} \tag{19}$$

where a = the order of the reaction,

$\quad B$ = a constant representing the "energy of activation," and

$\quad C$ = a constant of integration,

from which it may be shown that for any given pressure (P), k has a maximum value when $T = \dfrac{B}{a-1}$.

Thus the well-known fact that the rate of flame travel (32), as well as the rate of rise of pressure (4, 21), may be decreased by an increase in initial temperature may be explained on the basis of the well-known effect of temperature and density upon gaseous reactions.

Combining equation 19 with 18

$$\frac{dP}{dt} = C\frac{h}{C_v}\left(\frac{P}{T}\right)^a(e)^{-\frac{B}{T}} \tag{20}$$

By means of this equation it has been shown (4) that there is a real positive value for the initial temperature (T) which will give the maximum rate of rise of pressure upon explosion of an explosive mixture for any given constant initial pressure, P, and if the order of the reaction, a, is greater than 1, the same statement applies to mixtures which may be ignited under conditions of constant initial density.

Similar relationships leading to exactly the same conclusions can be derived by a more complicated procedure, assuming normal combustion or progressive inflammation by a self-propagating flame

These conclusions have been verified by experimental work in bombs (4, 21). Furthermore, the effect of heat capacity of the products of combustion and of their change with temperature upon the relative value of the initial temperature giving maximum rate of rise of pressure, has also been confirmed experimentally (21) in bombs The general conclusions regarding the "critical initial temperature" giving maximum rate of rise of pressure have also been confirmed by tests conducted in normal and supercharged engines (21)

It is therefore indicated that the same thermodynamic or macroscopic approach may be used with satisfactory results in problems involving rates as well as those supposed to be at equilibrium.

APPENDIX II

NUMERICAL CALCULATIONS USING THESE EQUATIONS DERIVED ON THE ASSUMPTION OF IDEAL GASES

If $K = 1\ 3$, $P_1 = 160$, $P_2 = 760$

(1) Compute Q (B t.u per cubic foot at $P_1 T_1$): by equation 4, since $V_1 = V_A$

$$Q = \frac{P_2 - P_1}{K - 1} = \frac{(760 - 160)144}{(778)(0.3)} = 370 \text{ B T U}$$

(2) Calculate the ratio of the final volume of the last portion to burn to its initial volume. from equation 4

$$Q(K - 1) = P_f - P_0$$

and $P_c = P_f$. Equation 8 becomes

$$V_{fL} = \frac{(P_f - P_0)V_0}{P_f K} + \left(\frac{P_0}{P_f}\right)^{\frac{1}{K}} V_0$$

$$\frac{V_f}{V_0} = \frac{600}{760 \times 1\ 3} + \left(\frac{160}{760}\right)^{\frac{1}{1\ 3}} = 0\ 608 + 0.307 = 0\ 915$$

(3) Calculate the ratio of the final volume of the first portion to burn to its initial volume. When

$$P_c = P_0$$

$$V_{fI} = \frac{(P_f - P_0)V_0}{K(P_0)}\left(\frac{P_0}{P_f}\right)^{\frac{1}{K}} + \left(\frac{P_0}{P_f}\right)^{\frac{1}{K}} V_0 = \left(\frac{P_0}{P_f}\right)^{\frac{1}{K}} V_0 \left[\frac{(P_f - P_0)}{KP_0} + 1\right]$$

$$\frac{V_f}{V_{0_I}} = \left(\frac{160}{760}\right)^{\frac{1}{1\ 3}}\left[\frac{600}{160.13} + 1\right] = 0\ 307\,[3\ 88] = 1\ 19$$

Since this is an ideal gas and the initial temperature T_0 was the same for all parts of the mixture and V_0 was likewise the same, it follows that

$$T_{fI} = T_0 \times \frac{P_f}{P_0} \times \left(\frac{V_f}{V_0}\right)_I$$

If $T_0 = 1150°$R., $T_{fI} = 6500°$R., $T_{fL} = 500°$R.

(4) Assuming that the last third of the charge burned were to "detonate" and that the quantity of charge burned normally is directly proportional to the increase in pressure in normal combustion, the final pressure after equalization may be computed by equation 14 or 14a derived on the assumption that the working substance is an ideal gas

$$P_z^{\frac{1}{1\,3}} = \left[\left(\frac{560}{160}\right)^{\frac{1}{1\,3}} - \frac{1 - \left[\left(\frac{760}{160} - 1\right)\left(\frac{160}{560}\right)^{\frac{0.3}{1.3}} + 1\right]^{\frac{1}{1\,3}}}{\frac{760}{160} - 1}\left(\frac{760}{160} - \frac{560}{160}\right)\right]160^{\frac{1}{1.3}}$$

$$= \left[2\,621 - \frac{1 - (3\,75 \times 0\,75 + 1)^{\frac{1}{1.3}}}{3.75}(4.75 - 3\,5)\right]160^{\frac{1}{1\,3}}$$

$$= \left[2\,621 - \frac{1 - 2\,797}{3\,75}\,1\,25 = 3\,22\right]160^{\frac{1}{1\,3}}$$

$$= 159.5$$

$P_x = 730$

This represents a loss of 30 lb out of 600 lb. pressure rise, or 5 per cent.

(5) Compute the compression ratio (r_2) that would cause the last third of the charge to detonate if the compression ratio of r_1 is just insufficient to cause incipient detonation

From equation 4

$$Q(K - 1) = (P_b - P_1)$$

For adiabatic compression

$$\frac{P_1}{P_0} = \left(\frac{V_0}{V_1}\right)^K = (r_1)^K$$

For incipient knock

$$Q(K - 1) = P_b - P_0(r_1)^K$$

From which r_1 may be determined by substituting the numerical values

$$\frac{370 \times 778}{144}(0\,3) = 760 - 14\,7\,(r_1)^{1.3}$$

$$r_1 = 6.25$$

Substituting the numerical values in equation 17

$$760 = 14.7\,(r_2)^{1\,3} + \frac{600}{6\,25}\left(\frac{2}{3}\,r_2\right)$$

$$r_2 = 8.3$$

This corresponds to an increase in compression ratio of 33 per cent at 6.25 ratio to cause the last third of the charge to detonate as referred to the compression ratio just short of incipient detonation.

CHEMISTRY OF OTTO-CYCLE ENGINE COMBUSTION

HAROLD A. BEATTY

Ethyl Gasoline Corporation, Detroit, Michigan

Chemical study of internal-combustion engines is amply justified from the theoretical as well as the practical point of view. Aside from their obvious economic importance, engines have provided a wealth of information regarding the nature of combustion, much of it unattainable with other conventional forms of laboratory equipment. In return, the interpretation of these results has been—and to a large extent still is—a complex problem which challenges those chemists who are interested in the general theory of the subject.

Nevertheless, it seems fair to say that, until recently, there has been in general a lack of effective cooperation between the chemists on one hand and the engineers on the other, and advances in the theory of engine combustion have been slow. This seems to have been due largely to a tendency, on both sides, to oversimplify the problem. Chemists have made numerous laboratory experiments under conditions not remotely resembling those of an engine, but the results were applied, without criticism, directly to engine combustion, at the same time no detailed analysis has been made of the chemical facts furnished by the engine itself. On the other hand, engineers have been largely occupied with the practical development and testing of engines and fuels, with little or no direct investigation of the chemical theory of the subject.

Recent years have seen considerable improvement in these respects. Chemical experimentation conducted directly with engines or closely related apparatus has given a series of facts to replace uncertain assumptions; simultaneously, the development of the chain reaction theory of the slow oxidation and explosion of gases has provided a reasonable basis for the explanation of the phenomena observed. As a result, it is now possible to advance a general outline of the nature of engine combustion which is in accord with the known facts and appears to be theoretically sound. At the same time, a great many details remain to be filled in and a number of major points are still in doubt.

It is the purpose of this paper to present, briefly, such an outline, to indicate some of the respects in which our knowledge is still deficient, and

to emphasize further the relative complexity of engine combustion. It is hoped that this survey will to some degree promote better appreciation of the problem and encourage still more effective cooperation between the chemists and engineers who are concerned with it We shall consider in our survey only the Otto-cycle engine, since the Diesel engine will be dealt with in other papers of this symposium. No attempt will be made to refer to the extensive literature on the subject, either in its entirety or specifically.[1] Only those data and conclusions which have been instrumental in establishing our present conception of the subject have been selected; their interpretation is the present author's personal one, but appears to be in general accord with the consensus of opinion.

NORMAL COMBUSTION

Normal combustion in an engine comprises the spark ignition and subsequent slow inflammation of the charge, followed by equilibrium changes in the burned gas. Owing to the method of operation, the hydrodynamic and thermodynamic aspects are highly complex, but the chemistry appears to be no more complicated than that of the similar inflammations which have been investigated by various laboratory methods.

First, the air–fuel mixture, containing the slight excess of fuel required for development of maximum power, is mixed with more or less exhaust gas, compressed to over 5 atm., and ignited by the spark. The mechanism of this ignition is a specific problem, and has been considered in foregoing papers in this symposium. In the engine there appears an ignition lag, which may be defined as the period, following the initial spark, during which no reaction is detected visibly or otherwise. The lag is about 1 millisecond or less, and does not seem to vary greatly with the fuel used. This subject has not been studied in any detail, and might well repay closer investigation. It is obvious that reactions of some kind are taking place during the lag, and information as to their nature might be obtained from correlation of lags with other combustion characteristics of the charge, such as normal flame speed and knocking tendency.

The flame front then travels through the charge, accelerating rapidly to a speed of the order of 100 ft. per second, then slowing down near the end of its passage; it is highly irregular in shape, owing to turbulence. For the type of air–fuel mixtures used in engines, there is as yet no exact solution of the problem of flame speed; we can only assume that the inflammation is a chain-reaction process in which the interaction between the chain carriers and the reactant molecules requires a considerable energy of

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[1] For recent selected bibliographies see the appropriate sections of *Science of Petroleum*, Oxford University Press (1937), *Proceedings of the Second World Petroleum Congress*, Paris, 1937, and this symposium; also references 1, 2, and 3.

activation, that is, the fuel molecules are relatively stable and slow to react. Thus, ahead of the flame front, the chains are broken until the resulting general temperature rise furnishes the surplus energy necessary for further chain extension. Then the flame velocity is a function of such variables as the number of chain carriers emitted, their available energy, and the surplus energy of activation required. These quantities, in turn, are dependent, in order of increasing importance, on the pressure, temperature, and composition of the unburned gas.

In an engine these variables are continuously changing in the gas ahead of the flame front, and the flame velocity might be expected to show a regular increase as combustion proceeds. But these effects are not noticed, since the true mass or transition velocity is much less than the actually observed space velocity, owing to the turbulence of the charge. Hence, in engines, the visible flame speed is determined almost wholly by engine speed and the corresponding turbulence. Changes in composition of the charge, including dilution by exhaust gas, have some effect, variations in charge temperature and pressure have little or no effect, and the presence of small amounts of antiknock compounds is not noticeable.

Combustion of the fuel is practically complete within the narrow flame front; behind the flame front, as the temperature falls, shifts occur in the equilibria between the reaction products. The corresponding pressures and temperatures at different points in the burned gas have been experimentally determined, and are in accord with this mode of combustion. The pressure rise is smooth and noiseless; its maximum rate is of the order of 1000 lb. per in.^{2} $\times$ msec. The flame spectrum is normal, and shows the C—C and C—H bands.

ABNORMAL COMBUSTION

As the "severity" of engine conditions—the pressure, temperature, and heating time of the charge—is increased, the fuel no longer remains entirely inactive, but instead tends to react spontaneously in one way or another, leading to an abnormal type of combustion. The type obtained depends both on the particular engine conditions and on the chemical nature of the fuel. We distinguish, roughly, three different types: preignition, after-firing, and knock.

In preignition the charge, on coming in contact with some hot spot, such as the exhaust valve, ignites prior to passage of the spark, and if this occurs early enough in the cycle, there is back-firing into the carburetor. Some fuels, notably benzene and methanol, tend to preignite under the same conditions under which other fuels tend to knock. This distinction is not only of practical importance but has obvious significance in the theory of combustion. As might be expected, the addition of antiknock

compounds such as tetraethyllead has but a slight effect, often detrimental, on the preigniting fuels; the organic antiknock compounds have not been tested extensively. In this connection laboratory tests of ease of ignition by a hot wire or the like might prove valuable; the time of heating should be very short.

In after-firing the spark may be cut out and the charge continue to ignite by compression. It is not clear to what extent this phenomenon is a form of preignition or is a form of knock. It can be regarded as a sort of delayed preignition, but there may be some effect on adding an antiknock agent, depending on the type of fuel used; this might well be investigated in machines of the adiabatic-compression type where the operating variables, especially the temperature, can be better controlled.

Knock is a form of spontaneous ignition, starting at one or more points in the "end gas" or unburned charge ahead of the flame front. The amount of charge entering into knocking combustion may vary from an indistinguishably small portion to at least three-quarters of the whole; also, apparently, the intensity or rate of knock may vary considerably. The knock flame seems to sweep through the remaining unburned charge, with a velocity in the neighborhood of 1000 ft. per second,—a value far greater than that of the normal flame, but much less than would be calculated for a true detonation wave in similar air–fuel mixtures. Correspondingly, the rate of pressure rise is high, the maximum value being of the order of 10,000 lb. per ft.^{2} $\times$ msec., and the change in the rate of pressure rise is sufficiently abrupt to set up pressure waves, which induce the emission of sound waves from the engine. The spectral emission of the knocking flame resembles that of the normal flame, but it has a greater extent and intensity and the characteristic hydrocarbon C—C and C—H bands are weak or disappear. The normal flame prior to knock is indistinguishable from that observed in the entire absence of knock.

In non-knocking operation no indication is found of any extensive chemical change in the end gas. As conditions are changed in the direction to produce knock, formaldehyde appears in the end gas in increasing amounts, which may vary for fuels of equal knock intensity. Compounds of the peroxide type are also present, but the amount of oxygen consumed is small. Suppression of knock by addition of aniline eliminates the formaldehyde, but with tetraethyllead, it is stated, this effect is not obtained in the engine. Both antiknock agents suppress the formation of those unidentified compounds which, under conditions of incipient knock, give a continuous absorption in the spectrum of the end gas.

FACTORS IN KNOCK

By and large, any changes which increase the temperature, pressure, or heating time of the charge, or modify its chemical composition in the

direction of readier ignition, tend to promote abnormal combustion of one type or another. In the case of knock, any variations which would be expected to favor preflame oxidation of the end gas are found to promote knock. Because of its greater interest, subsequent remarks will be confined to the phenomenon of knock.

The relative importance of the time, temperature, and pressure factors is difficult to estimate, since they are not readily susceptible of independent variation in an engine and the functions relating these variables to the occurrence of spontaneous ignition remain entirely unknown for time periods as short as those in an engine. Recent work on spontaneous ignition indicates that the pressure as well as the temperature is an important factor, and it is to be hoped that further information will be obtained for shorter time lags. In the engine the pressure and heating time for the end gas can be quite accurately measured; the time is of the order of 1 to 10 msec. The temperature ahead of the flame has only been estimated approximately, but probably exceeds 500°C.; it will doubtless be desirable, later, to determine this more accurately.

Equally important in determining the onset of knock is the chemical composition of the charge, including the nature of the fuel, the air–fuel ratio, dilution with exhaust gas, and the presence of pro- or anti-knock compounds. The pronounced effect of the molecular structure of the fuel is well known, but the explanation of this effect is still far from complete. As to air–fuel ratio and charge dilution, it is difficult to determine to what extent these factors have a direct, chemical influence on the oxidation and ignition of the end gas, and to what extent they act indirectly by virtue of their effects on the velocity and temperature of the normal flame.

The influence of pro- and anti-knock compounds is conspicuous: as little as one molecule of tetraethyllead in over 200,000 molecules of hydrocarbon may be sufficient to give a noticeable decrease in knock. Proknock compounds usually either contain active oxygen or else react readily with air to yield it; some other compounds, such as certain bromides, are also effective. Antiknock agents are mostly metals or organometallic compounds, and a series of aniline derivatives. On a molecular basis the former are of the order of one hundred times as effective as the latter, the distinction being so marked as to suggest a fundamental difference in their modes of action. The relative and the absolute effectiveness of an antiknock agent may vary considerably, both for different fuels and for different operating conditions; for a given fuel the effectiveness is not directly proportional to the amount added, but tends to approach a limiting value.

In general, the characteristics of the knocking flame, particularly its spectrum, are the same, regardless of which factor—increase in time–tem-

perature-pressure, or change in chemical composition of the fuel, or decrease in the amount of antiknock agent—is responsible for its occurrence, and we conclude that all these factors are concerned with the initiation rather than the propagation of the flame.

The physical and chemical factors are often interrelated; thus the effect of a specific change in engine conditions is by no means necessarily the same for two different fuels, or for a given fuel with and without an antiknock agent added.

In addition there may be other factors, such as the effect of radiation or ionization from the flame front, the turbulence of the end gas, or the nature of the engine walls in contact with the end gas. These do not appear to be important; however, little is known about them, and it is quite possible that turbulence, in particular, may be a significant factor. There is as yet no particular evidence for the existence in the engine of surface effects of the chain-reaction type. The fact that such effects may be controlling factors in many slow oxidation reactions which have been studied by laboratory methods is no *a priori* reason for their importance in an engine, where conditions are widely different. The strictly thermal effect of surface, particularly of hot spots, is of course conspicuous.

THEORY

The foregoing facts readily suggest their own general explanation, and the hypothesis that knock results from a spontaneous ignition of the unburned charge was advanced at least thirty years ago. However, the lack of correlation between the knocking tendency and the spontaneous ignition temperatures of different fuels, alone or with antiknock compounds present, casts doubt on the correctness of the hypothesis. This doubt disappears when the meaning of the term "spontaneous ignition" is analyzed, and it is realized that relative values measured under one set of conditions, as in some specific laboratory method, cannot be applied to widely different engine conditions; any attempt to extrapolate such values to reach engine conditions is insecure, owing to the chain-reaction nature of the processes involved.

The general theory is, then, about as follows: Before the arrival of the flame front, slow oxidation occurs in the end gas by a chain-reaction mechanism. In normal combustion the amount of such oxidation is slight, and the products formed have no important effect on the subsequent inflammation. Doubtless the rate of such oxidation is not constant and increases with time, but before the ignition point is reached the arrival of the flame completes the combustion. When the conditions are such that knock will occur, then the rate of oxidation is greater, probably owing to greater efficiency of chain extension, and it increases until the critical

point is reached where the coefficient of chain branching becomes unity. There is then a sudden very considerable increase in the concentration of activated partial oxidation products in the end gas. It may be that this reaction itself is the actual ignition, and that the completion of the combustion and the appearance of flame take place in conjunction with it, throughout the charge. Or, as seems more likely, it may be that the partial oxidation reaction merely gives a mixture which is far more inflammable than the original mixture. Its combustion may then be abruptly completed, as another step, by a flame which starts from one or more favorable points and is able to spread at a rate far greater than normal; that is, the combustion may be regarded as a kind of two-stage process. Thermodynamically, these alternative modes of ignition—by local action or by a moving flame—are practically identical, and there is no essential chemical distinction between them; the important point is that in either case the ignition is a result of a sudden change in the chemical composition of the gas, and not of a final critical increment in temperature alone. If we grant the presence of a moving flame of knock, it seems reasonable to expect this to start from the normal flame front, where the available energy is greatest, and the photographs suggest that this does occur in many cases. But it need not do so, since the development of the preliminary branched-chain reaction is probably not uniform throughout the end gas, and as a result that part of the gas which first attains the condition of extra-inflammability and ignites, may be well removed from the normal flame front.

The occurrence of a moving flame having a velocity intermediate between that of the normal flame and that of a detonation wave is not an unreasonable hypothesis. Although the inflammability of the mixture through which the flame of knock passes has become much greater than normal, there is no particular reason to suppose that it attains the degree of inflammability necessary for the propagation of a detonation wave. Such intermediate flame velocities are not usually observed in combustion experiments in tubes, etc., for the obvious reason that no chemical changes take place in the unburned charge in those cases; however, abnormal flame velocities or quasi-detonations have been observed when the ignition source provides a high surplus of energy.

Any attempt to make the foregoing description of knock more specific by defining the exact nature of the chain reactions involved and the products obtained possesses considerable uncertainty. Specific reactions have been proposed to describe the results obtained in slow oxidation and ignition of gases carried out under conventional laboratory conditions, but the actual chemical analysis of these reactions is far from complete. For the more drastic engine conditions practically no actual facts are available, other than the afore-mentioned presence of formaldehyde and other un-

identified oxygenated compounds and the disappearance of the C—C and C—H bands in the subsequent inflammation. Correspondingly, any attempt to correlate the knock resistance of specific hydrocarbons with the mechanism of their slow oxidation is uncertain to the same degree, and there is as yet no sound reason for believing that the results obtained for these hydrocarbons under laboratory conditions can be applied to engine conditions without modification. The extent, if any, to which straightforward thermal decomposition of the fuel molecules influences the oxidation reactions preceding knock is unknown. It seems possible that differences in thermal stability may account for the variation in knocking tendency of some structurally similar hydrocarbons which would appear to be of approximately equal susceptibility to attack by oxygen. Investigations along this line are desirable.

The action of pro- and anti-knock compounds is, of course, readily explainable on the basis of this theory of slow oxidation by chain reactions in the end gas. But here again, the specific mechanism of their action remains almost entirely unknown. The organic antiknock agents are presumably destroyed in the act of chain-breaking. If this can be confirmed, it is possible that valuable information as to the number and length of the chains can be obtained from a quantitative study of the effects of these agents. There is a strong suggestion that the metallic atoms are able to break chains repeatedly, probably by virtue of alternate oxidation and reduction; it is reported that the absorption spectrum of the end gas shows atomic lead but no lead monoxide when knock is eliminated by the addition of tetraethyllead.

COMPLEXITY

The foregoing summary of the observed facts and general theory of engine combustion has failed to fulfil its purpose, if it has not sufficiently indicated the complexity of such combustion and given some indication of the chemical and mechanical problems which remain to be solved before a more detailed theory can be developed.

Actually, in engine studies, the principal variables under direct control are the speed, spark timing, and jacket temperature of the engine, and the pressure, temperature, and composition of the charge. As regards the end gas, any attempt to change one variable alone inevitably causes one or more of the others to change also, either directly, or indirectly by affecting the speed or temperature of the normal flame. Other factors, such as the turbulence and the nature of the combustion chamber surfaces, cannot be closely controlled during the progress of a run. The effect of such uncontrollable factors, or of slight variations in the controlled variables, leads to considerable irregularity in the combustion from one explosion

to the next. This is clearly shown, photographically and otherwise, even by engines operated under rigidly specified conditions; the flame speeds and temperatures, for example, may vary by as much as 5 or 10 per cent. This complexity makes both the correlation and the analysis of results very difficult.

On the other hand, laboratory experiments conducted in special equipment and under carefully controlled conditions so far have failed to come anywhere near duplicating engine conditions, and, as previously pointed out, the relations between the different conditions are uncertain to a high degree. For example, ignition temperatures may be measured in the conventional manner, with a time lag of one second to one hour or more, during which time it is supposed that a certain necessary amount of slow oxidation takes place, and relations may be established between the pressure, temperature, etc., and the time lags. But this slow oxidation during the time lag may itself also have an induction period (probably largely conditioned by the combustion chamber surfaces) of the order of, say, one millisecond. Then the effect of the pressure, temperature, etc., on this short time lag will be entirely overlooked in the laboratory experiment, but may be the paramount factor in the engine.

An analogous case occurs in Diesel combustion, where it can be shown that the flame starts in the vapor envelope surrounding the fuel spray, after a time lag whose origin is largely chemical and is not merely the time of evaporation and heating of the vapor. The dependence of this time lag on the pressure and temperature is by no means a linear or simple function.

An even worse situation arises when we have the possibility of simultaneous reactions, with different pressure or temperature coefficients, and this probably is the case in the slow oxidation of the higher hydrocarbons. A further complication is that under certain conditions such reactions have a negative temperature coefficient over a certain temperature range. To what extent this effect applies under engine conditions is uncertain, but there is evidence that under some conditions an increase in temperature may reduce the possibility of knock, while increasing that of after-firing.

Examples

The result of this engine complexity is well illustrated by the ambiguity which arises in determination of the absolute or relative knock ratings of different fuels or pure hydrocarbons. An example of the magnitude of the variations which can be obtained for two pure structurally similar hydrocarbons is furnished by the following data from the recent results of S. D. Heron and F. Gillig of this Laboratory (1). The data give the effects of engine speed and jacket temperature on the *ratio* of the maximum power

output obtained from diisobutylene to that from isoöctane (2,2,4-tri-methylpentane), when run in a supercharged test engine, with the inlet pressure increased until the fuel fails by giving abnormal combustion. At 900 R.P.M. this power ratio falls from 1.64 at a jacket temperature of 212°F. to 1.01 at 350°F ; at 1800 R.P.M. the corresponding ratios are 0.90 and 0.82. Thus these moderate changes in engine conditions can effect a twofold change in the ratio of the power outputs. Many other similar examples are available, but have received little or no attention from the chemical point of view.

On the other hand, as is well known, chemical information of a comparative nature, which is relatively free from the effects of changing engine conditions, is provided by the ratings of fuels of different structures and by their response to antiknock compounds. Such results need not be confined to hydrocarbons of the gasoline type, but may be extended to other compounds, with possible added significance for combustion theory. An example is furnished, through the courtesy of S. D. Heron and F. Gillig, by their unpublished results for a series of propyl derivatives tested as above, at 900 R.P.M. and 212°F., alone or with 3 cc. of tetraethyllead per U. S. gallon. The respective power output ratios, relative in each case to unleaded isooctane, are as follows: n-propyl alcohol, 1.29 and 1.23; isopropyl alcohol, 1 54 and 1.56; 91 per cent isopropyl alcohol, 1.63 and 1.64; propylene oxide, 0.82 and 0.88; acetone, 1.72 and 1.78; diisopropyl ether, 0.92 and 1.05. The marked lead response of the ether, and the slight response, if any, of the other substances appears chemically significant.

This brief survey shows what type of knowledge has so far been obtained regarding the mechanism of combustion in an engine. It also indicates how the complexity of the problem accounts for the scantiness of definite information. Decided inroads are being made by the groups of investigators attacking the problem from various angles. Their realization of the difficulties encountered and of the necessary slowness of progress, coupled with their caution in drawing conclusions after each advance is made, bids fair for definite achievements and possibly for an ultimate solution of this extremely delicate and important chemical problem.

REFERENCES

(1) HERON, S D., AND GILLIG, F.: Second World Petroleum Congress, Paris, 1937.
(2) VON ELBE, G., AND LEWIS, B : Ind Eng. Chem. **29**, 551 (1937).
(3) WITHROW AND RASSWEILER: Ind Eng. Chem. **28**, 672 (1936); S. A E. Journal **39**, 297T (1936).

THE COMBUSTION PROCESS IN THE DIESEL ENGINE

G. D. BOERLAGE AND J J. BROEZE

N V. de Bataafsche Petroleum Maatschappij, The Hague, Holland

INTRODUCTION

The Diesel engine is characterized by injection of fuel in the combustion chamber and by self-ignition. Both characteristics give rise to typical problems. The former characteristic, i.e., injection of the fuel with subsequent formation of a combustible mixture, is the fundamental one.

This mixture formation immediately preceding combustion and continuing during combustion introduces the element of heterogeneity of the mixture to an extent unknown in gasoline engines. As a matter of fact, one is faced in the Diesel engine with mixture elements varying from pure liquid globulae and deposits to fuel vapors and pure air, the condition of this heterogeneous complex changing with tremendous rapidity, owing to agitation, evaporation, and combustion. As a result, conditions are always elusive; for instance, the strength of the mixture and the temperature of the flame vary continually throughout the charge.

This heterogeneity has its advantage, for it allows one to vary the load down to zero solely by regulating the fuel input, which is the cause of the excellent economy of the Diesel engine under varying load. That, however, is the only advantage. Most drawbacks of the Diesel engine do come from this very heterogeneity of the charge, the most obvious one being the impossibility of burning efficiently a quantity of fuel corresponding to the full amount of oxygen available in the cylinder, so that the power output stays behind that of an efficient gasoline engine. A second drawback, but in practice often the more important one, is the great tendency of the Diesel engine towards incomplete combustion, causing internal troubles as well as dirty and foul-smelling exhaust gases.

Figure 1 represents schematically the charge in a Diesel engine at a phase of its combustion process. Figure 2 represents schematically and comparably the charge in a gasoline engine; the difference in simplicity of conditions as compared with figure 1 is obvious.

This heterogeneity may be put forward as an excuse for the still existing lack of precise knowledge concerning the Diesel process, now that the Diesel engine has reached its fortieth anniversary. Whereas today the

knowledge of the combustion process of the gasoline engine has developed
to a point where quantitative results of general validity can be foretold,
that of the Diesel engine allows only an acceptable qualitative analysis.
For the first two decades the process of the Diesel engine was only a con-
fused picture, in which chemical and physical considerations, ignition and
combustion phenomena, space and time were all mixed up.   A. Riedler (3)
was one of the first to try to disentangle the various elements of the prob-
lem.   He suggested the following picture of the stages of the combustion
process: (*1*) introduction of the fuel, (*2*) atomization, (*3*) evaporation,
(*4*) mixture formation, (*5*) decomposition, and (*6*) combustion.   It is in-
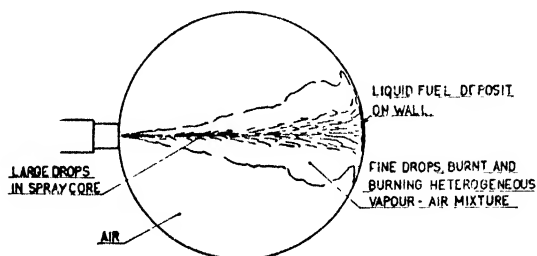
FIG. 1. Diesel engine combustion process schematized
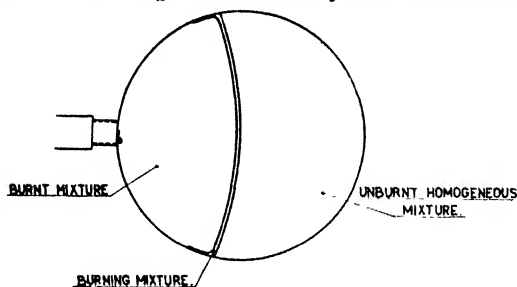
FIG. 2. Gasoline engine combustion process schematized

teresting to note that these stages, which Riedler visualized as being sub-
sequent in time, actually do exist but overlap each other considerably.
   Before starting to analyze the Diesel process, the authors wish to make
two statements: first, that for many reasons (e.g., difficulties due to the
heterogeneity mentioned before) the insight available today concerning the
Diesel process is due more to mechanical and physical than to chemical
research.   In this respect it may be useful to state that the authors, as
mechanical engineers, have had the full collaboration of physical and
chemical scientists; they admit, however, that it is possible that they have
stressed the mechanical aspect of the problem rather much.   Second, that
they intend to give in this exposition only their personal views on the

subject with no more than the necessary references to contradictory opinions, a fairly complete reference to the current status of research may be found in their contribution on the same subject in the recently published encyclopaedia *Science of Petroleum*

ANALYSIS OF THE DIESEL PROCESS

A Mixture formation

A perfectly combustible mixture is conceivable only with fuel in the vaporized state, the vapors being homogeneously mixed with the air and in such proportion that every bit of fuel and oxygen can be consumed The fact that the mixture in the Diesel engine is imperfect in all these respects adversely affects, among other things, the progress of combustion Now combustion, to be most efficient, should occur when the piston is near its top dead center, if part of the fuel burns later, the combustion process will be the less efficient for it Consequently, the more time in the course of combustion is taken up to correct a certain imperfection of the mixture, the more serious this imperfection is

The mixture presents two aspects of structure (*1*) Microstructure, pertaining to the size of the particles of the fuel and to whether these particles are in liquid form or vaporized, all considered locally, without regard to the condition of overall distribution of the fuel throughout the combustion chamber, and (*2*) macrostructure, pertaining to the condition of overall distribution of the fuel throughout the combustion chamber, without regard to the size of the particles of the fuel or whether these particles are in the liquid form or are vaporized

A good microstructure is obtained by first making drops of small sizes, which then quickly evaporate in contact with the air, with the combustion gases, or with the hot walls In the early air-injection engines these small drops were actually formed inside the atomizer, where a blast of air of high velocity acted on the surface of the fuel fed into the air stream, only very fine drops entered the combustion chamber In today's solid-injection engines the droplets are formed not inside the atomizer but almost entirely in the combustion chamber itself, owing to high pressure jets entering at high velocity (over 1000 m per second) and impinging on the dense air in the chamber (Here the name "atomizer" for the injector is actually misleading.) The mechanism of this atomization has been adequately dealt with by the National Advisory Committee for Aeronautics, by researchers at the Pennsylvania State College, and by others in very excellent pieces of research work Figure 3, taken from Report No 454 of the National Advisory Committee for Aeronautics, illustrates the mechanism of atomization in the clearest way

In order to obtain small drops the injection pressure and air density should be high, the orifice of the injector small, and fuel viscosity low. As soon as the velocity of the drops relative to the air has decreased appreciably, no further splitting up occurs and the next stages of preparation of the micromixture are provided for by evaporation and dispersion of the vapors in the immediate surroundings. There has been, and probably still exists, considerable divergence of opinion as to how fast droplets of the sizes considered (0 01 0 03 mm) do evaporate. Our opinion is that this process is exceedingly rapid, especially so once the combustion has set in and gas temperatures have risen from 600° to 800°C to over 2000°C

| At the nozzle | 1 inch from nozzle | 3 inches from nozzle |

| 5 inches from nozzle | 7 5 inches from nozzle | 10 inches from nozzle |
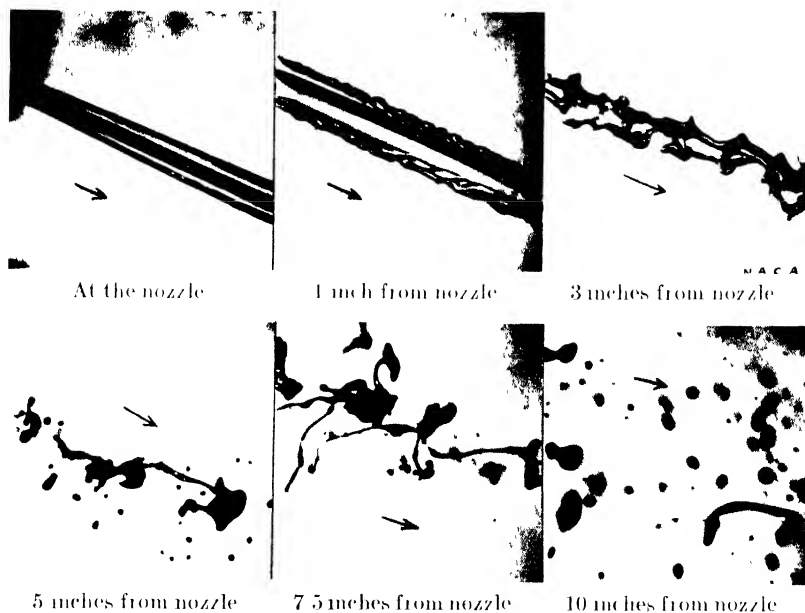
Fig 3 Micrographs showing process of atomization (N A C A)

Rothrock and Waldron (4) have shown that fuel sprays dissolve in 1 to 2 milliseconds even before ignition, after the flame has started a fraction of that time may be nearer the truth, which corresponds to only a few degrees "crank angle" even at an engine speed as high as 3000 R P M In the flame, therefore, one may consider evaporation as almost instantaneous

Spreading of the fuel vapors, as they are formed, into the wake of the droplets is effected by indiscriminate turbulence produced by the progress of the droplets through the air, and furthermore by diffusion Though very little is known about this spreading, it seems that the reach of diffusion

is small, but that its function must be important for the final molecular mixing.

In the early stages of the solid-injection engine, it had been found that the microstructure, however important, was not the biggest problem; experiments with extremely fine atomization led to disappointment. The cause of this disappointment was not clear at first, since the success of the air-injection engine had been attributed precisely to its finer atomization. As we will see further on, it was not so much the finer atomization, but the very efficient distribution (macrostructure) in the air-injection engine that caused this success. Now, with solid-injection engines, the finer the atomization, the more difficult it is to get good distribution.

Here we come to the important point of the macrostructure. The macrostructure is performed by injecting the fuel, in one or more sprays, into the air; this results in a structure as shown in figure 1, with great agglomerations of fuel here and pure air there. In order to get quickly a good, that is homogeneous, macrostructure, the relative motion between the heterogeneous portions of the charge must be increased, which explains the importance of turbulence. Turbulence, having done its part for the formation of a homogeneous macrostructure, turns over the job to diffusion again for final microstructure formation.

There exists a great diversity in the ways in which turbulence is applied in practice, for its type, energy, and origin may be vastly different; this diversity corresponds to the large variety of combustion chamber designs on the market.

The various types of air movement in combustion chambers are mainly: (a) indiscriminate turbulence, i.e., disorderly eddies with relatively small radii of gyration, which gradually disperse the clouds rich in fuel vapor; and (b) air swirl, i.e., orderly movement of the air in large orbits throughout the combustion chamber. This swirl may have two functions: the first one to "scrub" or "winnow" the fuel jets that are sprayed through the moving air, thus removing the vapors and finer drops; the second one, to act as stated above, viz., to carry parts of the charge bodily through the chamber and let indiscriminate turbulence, evaporation, diffusion, etc., finish the work in some other part. The varieties and combinations of these main types are almost endless.

Air swirls are applied, showing speeds varying from case to case, between virtually zero and a hundred or more meters per second, illustrating the range of appreciation that these swirls enjoy among designers. There are good reasons for this difference of appreciation: however useful the swirl may be to attain a good macromixture, at the same time it increases the heat transfer to the cylinder walls, and thereby the heat losses; furthermore, too fast a swirl may throw (or centrifuge) fuel out onto the walls,

thus overshooting the target.   Some designers, therefore, prefer to aim at good distribution by injection only, sometimes applying a swirl only as strictly required to correct insufficient distribution by the spray.   They try to fit the combustion chamber around the (often only alleged) shapes of one or more sprays (cf. figure 4), but since distribution is so heterogeneous in a spray, they have to allow for a relatively large excess of air. Although the power output is thereby restricted, the reduced heat losses may ensure a higher efficiency; thermal stress conditions of engine parts (cylinders, cover, piston) may be excellent.   Of course, injection should function excellently for this design.
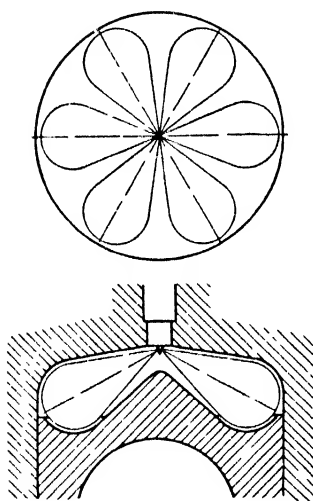
FIG. 4
FIG 5
FIG 4. Combustion chamber adapted to external shape of sprays
FIG 5. Induced air movement; four-stroke and two-stroke
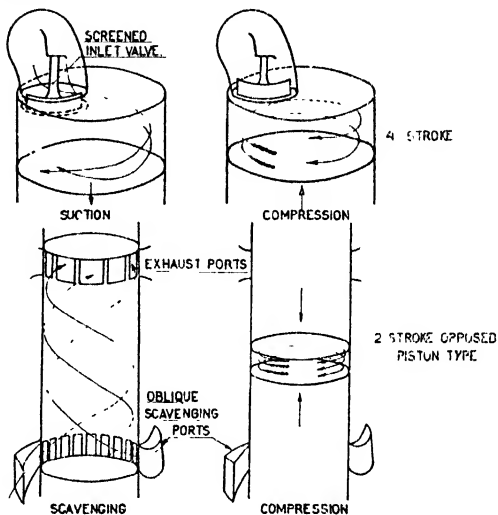
Other designers, though, with the idea of simplifying the functions of the injection equipment, prefer to aim at distribution by the air movement only; this solution may result in a somewhat greater reliability, a higher output, and, generally speaking, a better speed flexibility, but it involves a somewhat lower efficiency and a somewhat greater heat stress.

All kinds of compromises between these extremes exist, and usually the respective advocates of each system are most emphatic in their claims.

According to their origin, one may distinguish between induced and forced air movement.   Induced air movement is such movement as is caused by the entry of the air in the cylinder.   This will always produce indiscriminate turbulence, but by means of special valves or ports orderly swirl may also be set up (see figure 5).   Forced air movement is such

movement as is caused by the transit of the air from the cylinder to the combustion chamber during compression. This may also be indiscriminate turbulence and/or swirl (cf. figure 6)   Combination of both induced and forced air movement also exists (see figure 7).   Finally, movement of combustion gases may be caused by the combustion itself.

The allowable velocities of induced air movement are restricted, as too high velocities would hamper the breathing of the engine; that of forced air movement is limited on account of pumping losses, yet forced air movement may be, without objection, much more intense than induced air movement.   The use of either movement is limited on account of heat loss and of "fuel-throwing" ("out-centrifuging").

Movement of combustion gases as mentioned may be ensured in particular by starting combustion in a separate chamber, such as a precombustion chamber (cf. figure 8); the combustion in the prechamber
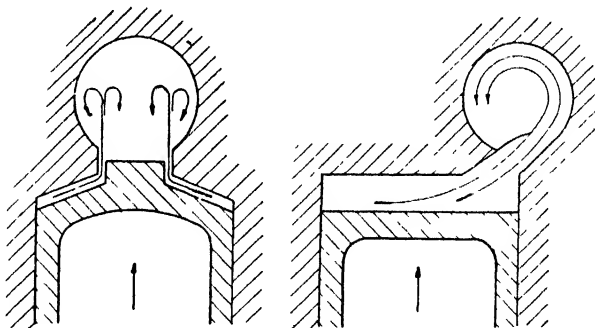
FIG 6   Forced air movement; turbulence and swirl

causes an increase in pressure by which the gases are blown into the main chamber.   Again, the design of the arrangement may be such that either indiscriminate turbulence or orderly swirl is predominant.   This combustion gas movement, though very efficient in many instances, is under less direct control than the two first-mentioned air movements, which depend wholly on the design, whereas the combustion gas movement depends also on the behavior of the primary combustion.   Here it is the experimental work on the test bench that carries the burden of finishing the design, but it may result in a construction which performs as satisfactorily as that of the air movement type.

The winnowing action of air movement on a spray depends *inter alia* on the structure of the spray and its rate of evaporation.   The spray usually consists of a core of rapidly travelling "chunks" of oil which are gradually stripped down to fine drops, and of a mantle consisting of drops so fine as to have lost their velocity.   The degree and rate of atomization

of the fuel influence the penetration and dispersion of a spray; the finer the droplets, the greater relatively the resistance of the air, that is, the shorter the penetration, but the greater the dispersion will be. Intense atomization makes the spray blunt or "soft," and makes it more susceptible to winnowing.

Low viscosity of the fuel as well as strong evaporation softens the spray and increases the amount of fuel removed by winnowing. The moment of ignition is therefore of great importance, since at that moment the rate of evaporation changes, as we have seen before, affecting spray softness. Therefore special study on the behavior of unignited fuel sprays will not give quantitative results that apply to real engine operating conditions; this of course greatly complicates research and development work.

Besides these considerations there remains the question of liquid fuel being deposited on the walls, either directly by the jet or by the fuel being
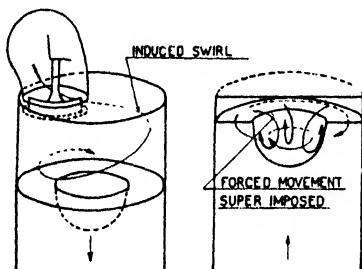
Fig. 7

Fig. 8

Fig. 7 Combination of induced and forced air movement
Fig. 8. Precombustion chamber principle
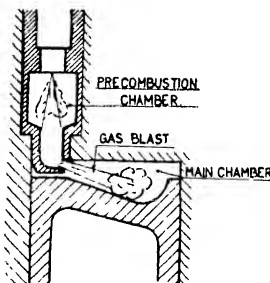
centrifuged out by air movement. These deposits are a typical imperfection of both micro- and macro-structures. For their combustion they have to be evaporated and then distributed by air movement. In the authors' opinion the liquid deposits form one of the biggest difficulties that have to be overcome in controlling the Diesel process; this difficulty is greatest either when using low-volatility fuels such as residual fuels or with small engines (on account of the small free space for the sprays). A carefully established balance between air movement, combustion gas movement, and wall temperature is necessary to get rid of these deposits. In general, high wall temperatures are extremely useful. In some cases where the air movement is small, it may happen that evaporation is too rapid for the amount of air passing over the spot, resulting in local over-richness. Usually, a large portion of the piston crown forms part of the combustion chamber wall, and so presents a relatively high temperature (up to 600°C.) right at the most important spots where the fuels jets

strike. If it be required to maintain such a high temperature in small engines, one has to resort to heat-insulated linings for the combustion chamber. In the absence of these hot walls, specially adapted fuels—without low volatility fractions—would have to be used, particularly in view of good combustion at part loads.

B. Self-ignition

If "ignition" in the technical sense may be described as "causing flame combustion," then "self-ignition" is the process of chemical reactions in the fuel-air mixture leading to flame combustion.

In the authors' opinion the best representation of the self-ignition process in the Diesel engine is as given in a previous paper (1) from which figure 9 is here reproduced. The fuel, whilst being injected and atomized, absorbs heat from the air and evaporates rapidly. The vapors, almost
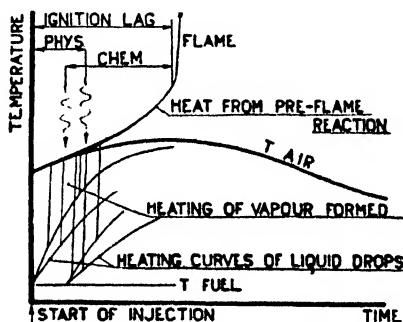
Fig. 9. Temperature during ignition

instantaneously attaining the temperature of the surrounding air (which locally may drop appreciably owing to this abstraction of heat, but is still of the order of 500° to 800°C.), enter into chemical reactions with the air, thus leading to locally increased temperatures; finally, in one or more spots where the conditions are most favorable, flame conditions will be reached. From these spots or flame nuclei the flame may spread with great rapidity. Of course a number of flame nuclei may have been born without growing to ripeness; these would-be nuclei are overtaken by the one or two more successful ones which will start the inflammation.

The evaporation effect has been shown by the afore-mentioned photographs of Rothrock and Waldron (4). Later experiments by Selden and Spencer (5) have shown the pressure drop due to the abstraction of heat. Large-scale pressure diagrams taken on Diesel engines may also show this pressure drop, but it is soon, often even immediately, overcome by the pressure rise due to the preflame reactions (cf. figure 10).

The time which elapses between the beginning of fuel injection and the reaching of flame conditions (or, as others have it, the beginning of rapid pressure rise) represents the ignition delay, which the authors have subdivided into (1) "physical delay," this being the period of the development of enough fuel vapor (endothermal part) to initiate the next period, and (2) the "chemical delay," this being the period required by the preflame reactions in order to reach flame conditions (exothermal part). The physical and the chemical delays cannot, of course, be entirely separated as to time, since considerable overlapping occurs. Still, physical and chemical delays must be, principally, considered as two separate phenomena; fuels of very low volatility show much longer total delays than could possibly be explained from their chemical character alone. For fuels of normal volatility the physical delay may be very small, probably between 5 and 10 per cent of the total delay; with residual petroleum fuels and also with some vegetable oils, it may amount to some 50 per cent of the total delay, the latter being thereby almost doubled.
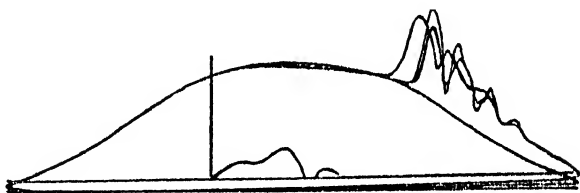
FIG. 10   Pressure drop during first part of delay.   Vertical line = beginning
of injection

It has been asked just what constitutes the most favorable conditions that lead to the formation of a flame nucleus. The answer is that one can only guess. Some experiments on self-ignition of vapor-air mixtures, by Peletier and Van Hoogstraten in the laboratory with which the authors are affiliated, are very interesting. For a C. F. R. gasoline engine that was being motored —with the ignition cut off—the investigators found that the lowest compression ratio which would cause a vaporized mixture to ignite by compression alone occurred with a mixture strength of 150 per cent of the theoretical value, and they found a similar value to hold for many fuels. This may be an indication that the flame nuclei in the Diesel engine are the spots where vapor-air mixtures of about such a composition exist; it may be assumed that fuel drops do not count in this respect.

During the same experiments (without sparks!) the heat development by preflame reactions could be clearly observed from indicator diagrams taken at a compression ratio just below the critical point (see figure 11);

this heat development by preflame reactions was also proven by the fact that the torque required for motoring the engine would then fall off to nearly zero. The phenomenon was accompanied by luminescence and an extremely acrid smell. Approaching the critical point of self-ignition, inflammation followed gradually. Most probably this is what occurs locally and on a smaller scale in the Diesel engine in said would-be nuclei.

Having tried to grasp as far as possible the character of a flame nucleus, the further question that rises is: What is its size? Let us assume that a certain mixture strength does constitute the most favorable conditions for the formation of flame nuclei. Now, minute regions showing this very mixture strength must needs exist around every fuel droplet, since its
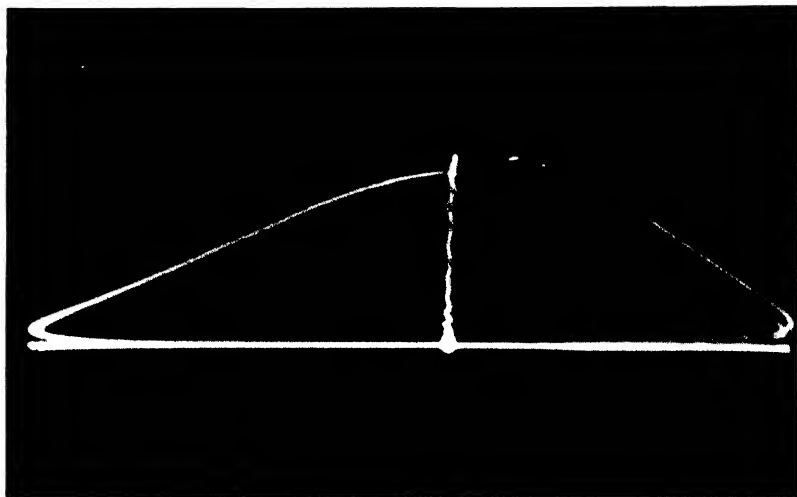
Fig. 11. Pressure developed by flameless reactions. Vertical line = top dead center position of piston

atmosphere contains all graduations from pure fuel vapor down to pure air. If these minute regions of most favorable mixture strength, or any single one of them, were capable of acting as centers whence flame spreads with great rapidity, then ignition delay would be entirely independent of injection characteristics, turbulence, etc., but it is not. The heat losses of such minute regions may be so great that it is impossible for them to reach flame temperature in so small a space. One is led to conceive of larger and stronger nuclei, characterized by a generation of heat that surpasses the heat losses to their neighborhood. The creation of these circumstances, i.e., nuclei sufficiently potent with respect to their surroundings, depends on many conditions, such as reaction velocity, temperature, and turbu-

lence   Turbulence in particular may influence the ignition delay, this
influence has been the object of many discussions and a few words about
it may be of interest

Turbulence enhances mixing and heat transfer   These combined in-
fluences affect the ignition process in different ways   first of all, they may
shorten the delay, owing either to an increase of the rate of heating of the
droplets, thus shortening the physical delay, or to the compensation of a
locally too large heat abstraction from the air, thus shortening the chemical
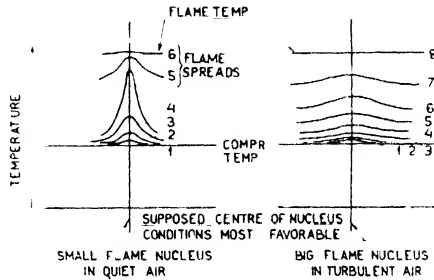
FIG 12 Nucleus formation in quiescent and in turbulent air schematized
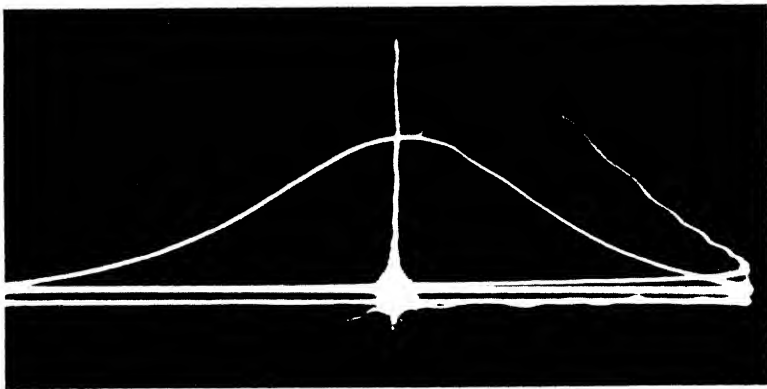
FIG 13   Diagram of combustion starting from a small nucleus (moderate
turbulence)   Vertical line = top dead center position of piston

delay   Therefore, in its first aspect, turbulence acts beneficially on the
delay   In its second aspect, however, the combined influences of turbu-
lence tend to lengthen the delay as soon as the local mixture temperatures
exceed the temperature of the surroundings the greater heat transfer tends
to cool the would-be nuclei   The mixing influence, moreover, tends to
decrease the local vapor-air ratio, which at first has no effect at all, as
long as there still remain regions very rich in vapor, but as soon as these
have been dispersed, the mixture becomes diluted below the composition

most favorable for self-ignition   Thus with strong turbulence both the increased heat transfer from the nuclei and this dilution of regions rich in vapor may lead to increased delays   Schematically these favorable and unfavorable influences may be illustrated by figure 12   Under favorable influences a nucleus may be, so to speak, of the size of a mere pinhead,
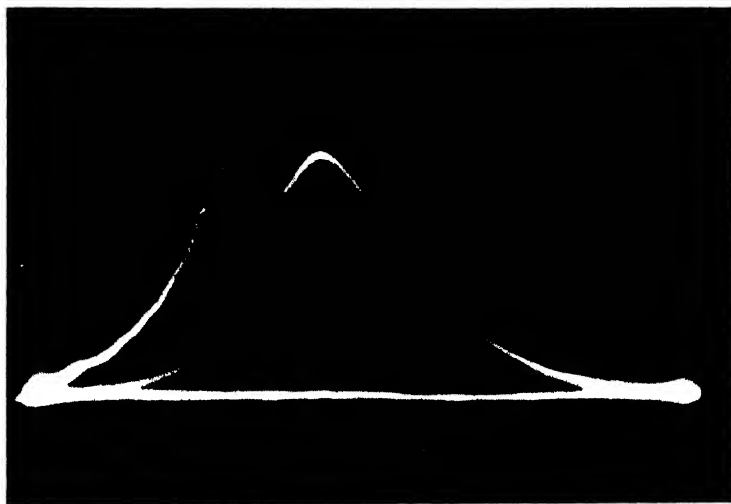
Fig 14 Diagram of combustion starting from a big nucleus (high turbulence), reading from right to left
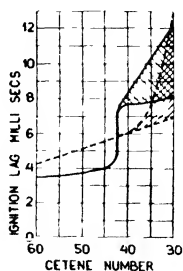
Fig 15 Delays in air-injection engine

the pressure diagram will deviate only very little from a straight compression diagram, up to the moment where pressure begins to rise rapidly (cf figure 13), owing to combustion, under unfavorable influences there may be formed a nucleus of much larger dimensions (cf. figure 12), a gradual extra pressure rise of several atmospheres may have been produced

by preflame reactions in a large portion of the charge, before, finally, combustion proceeds rapidly (cf figure 14)   (The two diagrams shown on figures 13 and 14 are taken on a low-turbulence and a high-turbulence type of engine, respectively)   The following experiments on an air-injection engine appear to show both favorable and unfavorable influences of turbulence (figure 15), low blast air pressure (45 atm) giving low turbu-
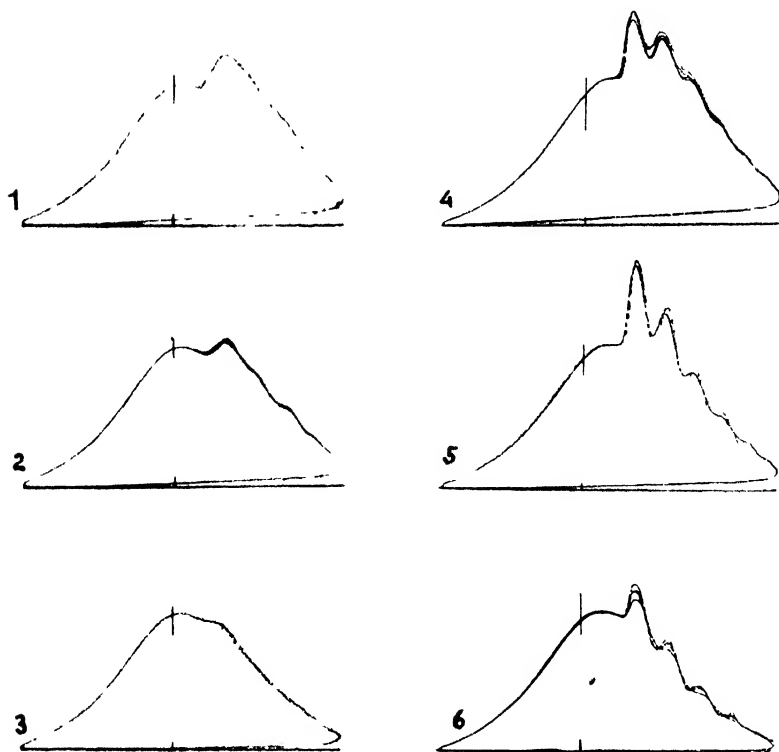
FIG 16   Diagrams showing decrease in combustion velocity with decreasing load in air-injection engine (1, 2, 3) and high combustion velocities in solid-injection engine (4 5, 6)   The short vertical lines show the beginning of injection

lence, and higher blast air pressure (60 atm) giving higher turbulence   For cetene numbers from 60 to 42, the higher turbulence gives shorter delays than the lower turbulence; between 42 and 30, however, the influence is just the reverse   (The cross-hatched area in the figure is due to unstable ignition conditions)

After having shown the influence of turbulence in dispersing regions rich in fuel vapor and the possible effects therefrom on ignition delay, we

shall now briefly discuss some further effects on the rate of burning
Figure 16 shows how turbulence affects, through the rate of burning, the
shape of the pressure diagram of a given engine (which was equipped for
either air injection or solid injection) for different loads, that is, for different
fuel air ratios   It will be seen that when using air injection the rate of
burning drops appreciably with the load, which is due to increasing leanness
of the mixture   When using solid injection, on the other hand, and for
about the same delay values, the rate of burning is better maintained when
the load is decreased, which is due to the more localized fuel distribution
through the charge   Of course, in the solid-injection engine also the rate
of burning may eventually become insufficient, owing to the delay be-
coming extremely long, as shown in figure 17   One must keep in mind the
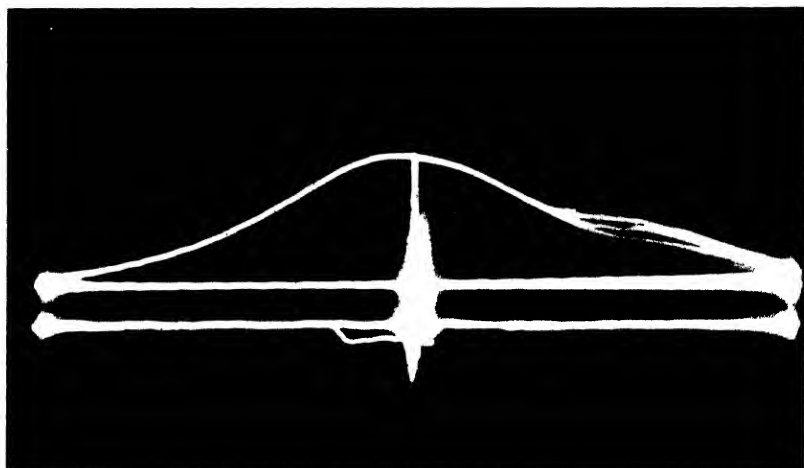
FIG 17 Effect of extremely long delay in solid-injection engine

hypothetical character of the above-mentioned considerations, the ways
and means of direct observation, which would give better evidence, fail at
present

Such is also the case when it comes to an investigation of the chemical
side of ignition   The ignition process is short (0 001 to 0 005 sec), and as
most chemical hypotheses have been derived from experiments made under
conditions entirely different from the actual process, it always has to be
proved over again that the conclusions hold good   The three main hy-
potheses are the following (1) fuel molecules combine with oxygen directly
(oxidation theory), (2) fuel molecules form unstable peroxides which
decompose exothermally (peroxide theory), (3) fuel molecules tend to
crack and become thereby abnormally sensitive to oxygen, or they do

C Combustion stages

In principle, four combustion stages may be distinguished, as seen from figure 18, which shows, by means of a schematic pressure diagram, the following combustion stages (1) delay, (2) inflammation of the fuel present at that moment, (3) injection-controlled combustion, burning of fuel injected into the flame, and (4) after-burning of all the fuel that has not yet found its oxygen or of which the burning rate had been too low (weak mixture, chilling)

Comparison with the ideal diagram, also given in figure 18, where every bit of fuel would be burned immediately as it enters the combustion chamber, reveals that there are mainly two independent causes for combustion lagging behind namely, the delay and the after-burning, the former being caused through deficiency of reaction velocity, the latter mainly through deficiency of mixing   All variations on the schematic diagram are met with in practice
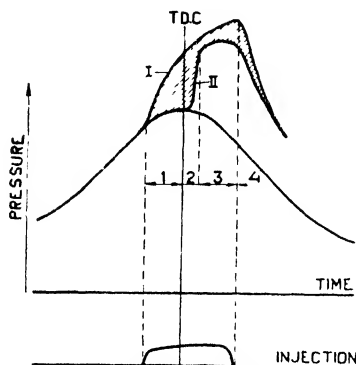
FIG 18 Actual and ideal pressure diagrams

D Physical and chemical aspects of combustion

1 Physical aspects

The purpose of combustion in the engine is the development of pressure, and the characteristics of the pressure diagram form the principal physical aspect of combustion.   Two requirements should be taken into account· (1) The development of pressure should occur as near the top dead center position of the piston as possible, having due regard to a reasonable maximum pressure   (2) The shape of the combustion pressure curve should be as smooth as possible, so as not to cause vibrations of the engine parts ("Diesel knock")   The control of the development of pressure would be entirely in the hands of the designer if the ideal diagram of figure 18 could be realized, the maximum pressure being controlled by suitable timing of

the injection Actually this is still the method of controlling the maximum pressure, but as the course of combustion depends *inter alia* on the type of fuel (viscosity, ignition quality, volatility) the maximum pressure may also vary with the fuel used, e g., to the extent of one to five atmospheres

In order to develop the pressure as near as possible to the top dead center, after-burning must be reduced to a minimum. It may be said that wherever fuel and air have been mixed in a proper ratio so that a high flame temperature is reached, the reaction velocity is high enough to satisfy the requirements as to restriction of after-burning for the highest engine speeds. The causes of after-burning, which have been mentioned above, may be summed up as follows

(*1*) *Inefficient mixing, in particular overrichness of parts of the charge* This tends of course to become the worse the greater the quantity of fuel,
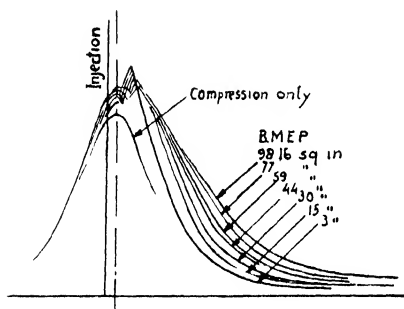
FIG 19
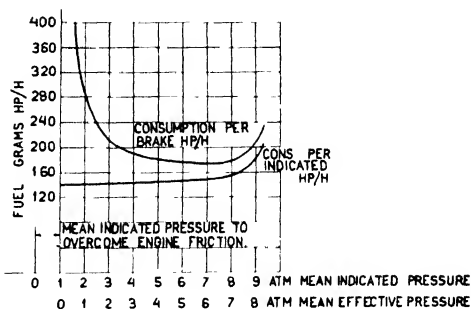
FIG 20

FIG 19 Diagram showing increased after-burning with increased load (Dicksee)
FIG. 20 Typical fuel consumption curves

but it depends fundamentally on engine design The influence of fuel quantity (load, brake mean effective pressure) is seen in figure 19, showing how combustion becomes more and more prolonged with greater loads. Consequently, the specific fuel consumption increases with the load. This is clearly shown by curves of fuel consumption per indicated horsepower-hour, i e , per unit of work done in the cylinder. (The consumption per brake horsepower-hour increases also for lower loads, but this is due to the decreasing mechanical efficiency (cf figure 20) and not so much to after-burning)

(*2*) *Deposits of liquid fuel on the walls of the combustion chamber.* This phenomenon is illustrated very well in figure 21, showing a photograph from N A C. A report No 545 by Rothrock and Waldron (4). At the spots where the fuel jets strike the walls, flames are seen to linger after the main combustion is finished This happened especially in the low load
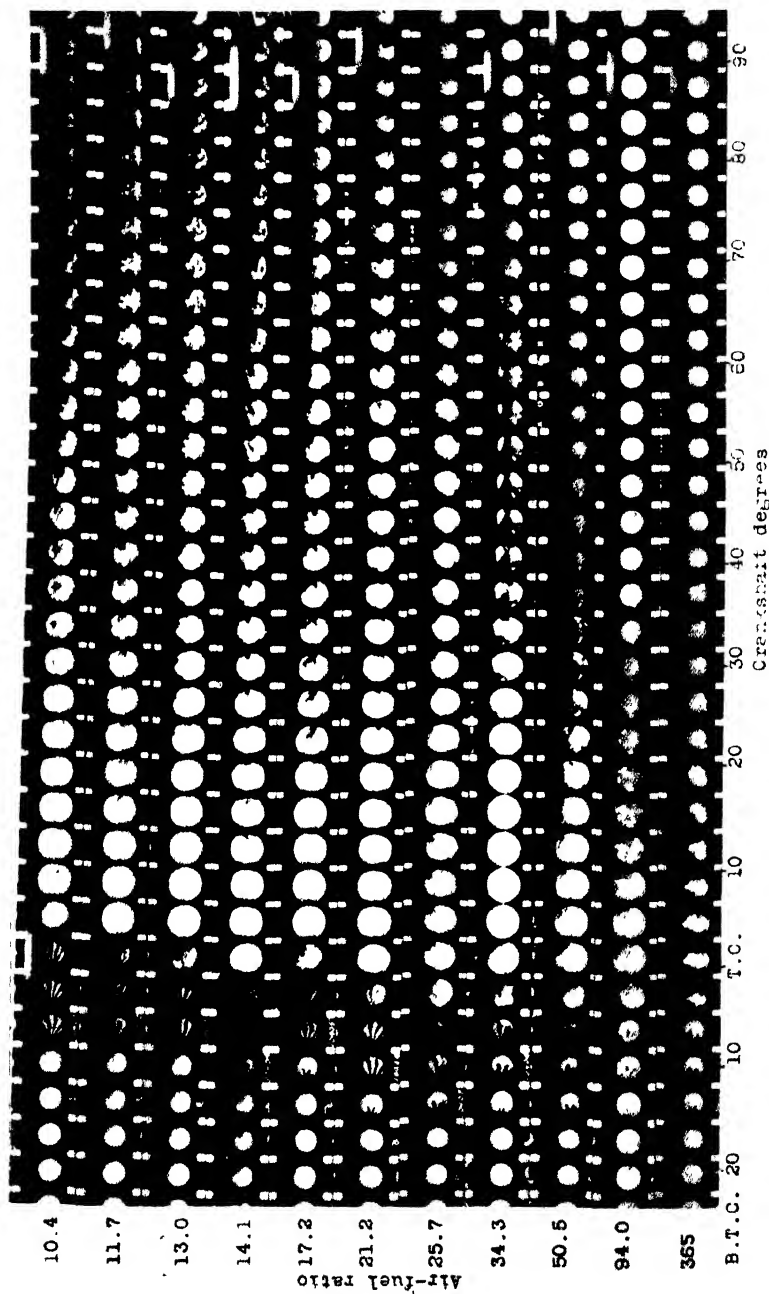
FIG 21 Photographs showing after-burning due to fuel deposits on combustion chamber walls at air-fuel ratio between 94 0 and 25 7 (N A C A).

zone (air–fuel ratio 25.7 to 94). Under higher loads the phenomenon became less clear, since then there were more causes provoking after-burning; with extremely small fuel quantities the sprays did not reach far enough to touch the walls. In practice, similar zones of joint load condition and after-burning due to fuel deposits may exist; it depends on numerous circumstances whether the trouble will be bad at all and if so, at which load. It usually will be more pronounced at the lower end of the load range, owing to poorer heat conditions and to longer delays, and especially owing to the low rate of evaporation   It is, however, certain that with heavy residual fuels it persists often over the entire load range and results then in a higher overall fuel consumption and a lower maximum power.

(*3*) *Long delays during which the fuel mixture has become lean throughout, resulting in low flame temperatures* (cf. figure 17)

Further there are still a few chemical causes.

(*4*) *Dissociation of the flame gases, especially at high loads, reducing the maximum flame temperature*   The degree to which this phenomenon participates in causing after-burning may be estimated as small in comparison with the phenomena mentioned above

(*5*) *Chilling of the flame near cool walls*   This will mostly accompany the second and third causes mentioned and would probably be quantitatively far less serious, but for the secondary phenomenon, that of leaving partially burnt products, which may accumulate in the engine

Of course, on first inspection of an engine and of its diagrams, it is not obvious which cause of after-burning prevails   Often experiments with fuels of different types may throw more light on the matter

From the foregoing it is evident that a fuel of low viscosity, high volatility, and high ignition quality will ignite easily but will tend to form localized overrich mixtures   High viscosity, low volatility, and low ignition quality will, on the other hand, cause a fuel to aggravate wall deposits and to form well-distributed mixtures, which may, owing to this good distribution, become too weak for rapid burning   The effect of a change of fuel on the efficiency of combustion may thus give some indication as to the most obvious cause for after-burning   Quite often, though, the various causes are so nicely balanced that the change of fuel has little effect, this does not imply at all that the engine is perfect.   An analysis of the composition of the partially burnt products may then be useful.

The shape of the pressure diagram is evidently greatly influenced by the delay.   The delay, followed by the subsequent inflammation, tends to give rise to one or two kinks in the pressure rise, where the rate of the pressure rise may change so abruptly as to cause vibration (audible as Diesel knock) and increased stresses in engine parts.   In a given engine the knock will usually increase with the delay, then decrease again (cf. figure 22).
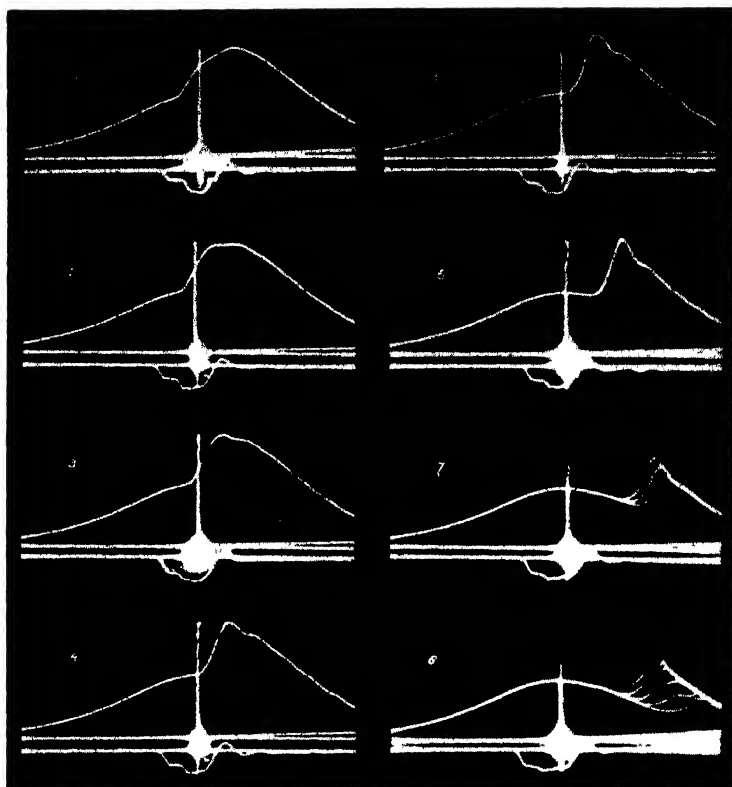
FIG 22 Series of diagrams with increasing delays (1 to 8)
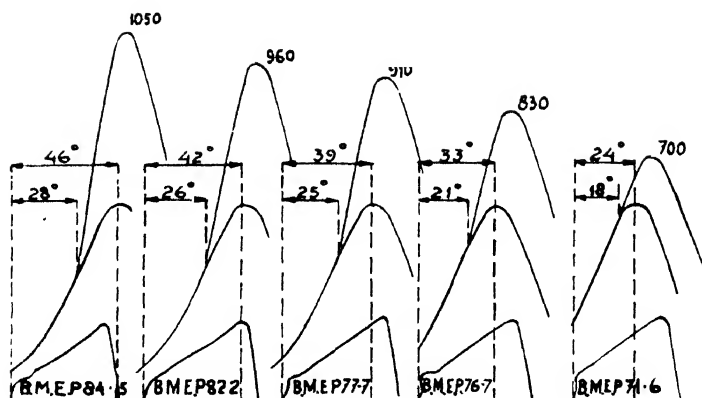
FIG 23 Smooth pressure rise notwithstanding long delays

The increase is due to the increase of the fuel quantities liable to explode with the delay and to the steadily improving distribution of the mixture; the decrease is due partly to the final weakening of the mixture which always occurs, and partly to the rapidly increasing volume of the combustion space. The state of turbulence during the inflammation period appears to have much to do with the rate of pressure rise, but whether this is due to improved mixing or to more rapid flame propagation cannot be made out. What the rate of pressure rise will be for a certain delay depends entirely on engine type, load, and speed (cf. figure 16). Thus some engines may have either short or long delays and yet remain smooth (cf. figure 23), whereas others will have a much more pronounced tendency to knock (cf. figures 13, 14). Therefore, although generally speaking a fuel of high ignition quality may decrease objectionable knocking in many engines in comparison to a fuel of low ignition quality, in other cases the effect may be less pronounced, and in still others neither of them will knock in an objectionable way.

2. Chemical aspects

The chemistry of the complex combustion occurring in a Diesel engine is far from being entirely known. The following material, which includes much of a paper presented last year (1), may be advanced as a crude outline of the general situation. Combustion of hydrocarbons may be, in principle, a direct oxidation (for instance, hydroxylation according to Bone and Wheeler) or a decomposition followed by oxidation of the destruction products (Aufhäuser's theory of destructive combustion). Haslam and Russell (2) came to the practical conclusion that generally both types of processes will occur side by side. When the fuel has been vaporized and well mixed with air before burning, the first type of reaction is most likely to develop, but when fuel vapor is suddenly exposed to high temperatures before mixing, the second type of reaction prevails. The conditions for the first type of reaction are met with in dry mixtures in gasoline engines, but in the Diesel engines there appears to be no doubt as to the conditions being more favorable for destructive combustion; the liquid fuel drops surrounded by flames form as many centers of vapor development, whereas the mixing process comes only afterwards. The characteristics of the direct oxidation process in mixtures of normal air–fuel ratio are as follows: blue flame (carbon dioxide and carbon monoxide radiation), no tendency to soot either from overrichness or from chilling, but production of carbon monoxide, aldehydes, and acids under chilling conditions. Characteristics of the destructive combustion process are as follows: radiant yellow-white flame ($C=C$ or black body radiation), and tendency to soot when locally

overrich and when chilled. Under overrich conditions carbon monoxide and hydrogen are formed by either process.

The evidence given by photographs of the flames, by exhaust color on overload, and by contamination of lubrication oil by soot, all point to destructive combustion as being predominant. Acrid exhaust odors, formation of carbon monoxide at low loads (see figure 24), and varnish-like deposits on pistons and in lubricating oil point to direct oxidation as part of the process, and are most noticeable under light loads and with long delays. This proves without further detail that actually both processes go on side by side

Chilling, due to cool walls, and dissociation (mainly of carbon dioxide) at high temperatures have been briefly mentioned as chemical causes of after-burning. When it is considered that a severe degree of contamination may be caused by incomplete combustion, due to chilling, of only a
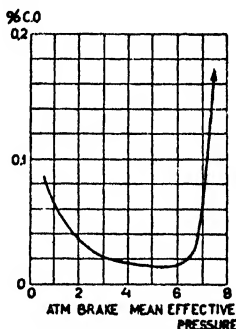
FIG. 24. Carbon monoxide content of exhaust gases

very small percentage of the fuel, it is obvious that the incomplete combustion of so little fuel will not materially affect the efficiency of the cycle.

From the foregoing it is seen that analysis of the products of incomplete combustion may be a guide towards a better understanding of the Diesel process. From a practical point of view these products hold one of the biggest problems in Diesel engine development.

Acrid smell and blue fumes from unburnt fuel are intolerable in road vehicles. It has been shown in a practical way that engine design may overcome them by allowing no fuel in the liquid state to come into contact with cool walls. Carbon monoxide is still more intolerable, but as the carbon monoxide content in Diesel exhaust gases is much lower than in gasoline exhaust gases, and as the latter generally are unobjectionable from a hygienic point of view, this is still more true in the case of the Diesel engine. A further effect of liquid fuel deposits may be carbonization, especially with residual fuels, leading to piston and valve troubles. Var-

nish-like deposits in quantities that will cause sticking of the piston rings within a short time are seldom encountered, but their influence at continuous operation may be severe enough, even if this influence be only the forming of binding material in crankcase sludge.

Stationary and marine engines usually have to be rated, on account of heat stresses, to low outputs, so that their exhausts may always be clear. In the case of vehicle engines, maximum output being required, the formation of soot limits the output, not only with regard to atmospheric conditions in the streets, but also because of the blotting paper action of the soot in drying up the cylinder walls, thus leading to piston troubles. Soot, furthermore, constitutes the greater part of the lubricating oil contamination.

REFERENCES

(1) BOERLAGE, G D., AND BROEZE, J. J.: Ind. Eng Chem. **28**, 1229 (1936).
(2) HASLAM, R T., AND RUSSELL, R. P : Fuels and Their Combustion, 1926.
(3) RIEDLER, A.: Löffler-Riedler, Oelmaschinen (1916).
(4) ROTHROCK, A. M., AND WALDRON, C. D : Natl. Advisory Comm. Aeronaut., Rept. No. 435 (1932).
(5) SELDEN, R. F., AND SPENCER, R. C.: Natl. Advisory Comm Aeronaut Rept. No. 580 (1937).
(6) TAUSZ, J., AND SCHULTE, F : Über Zündpunkte und Verbrennungsvorgänge im Dieselmotor (1924).

DISCUSSION[1]

A. M. ROTHROCK: Mr. Boerlage and Mr. Broeze are to be congratulated on their comprehensive survey of the combustion process in the Diesel engine. They have presented a clear analysis of their own and other researches. Papers presenting such an analysis are particularly valuable in that they permit general conclusions to be drawn from a mass of research and so prevent us from drawing erroneous conclusions from single researches.

In the third paragraph of the paper the authors state that the heterogeneity of the mixture in the engine permits the load to be varied down to zero solely by regulating the fuel input. Although we know, as shown by figure 21, that stratification of the charge does occur at low loads, we cannot be sure that in the Diesel engine such stratification is necessary. Gaseous combustion tests have shown that as the temperature of the gas is increased the limits of inflammability are also increased. With the ambient air at a temperature sufficient to cause the fuel to ignite in 0.001 sec. or less the number of ignition sources is infinite, so that each fuel droplet on vaporizing may act entirely independently of the surrounding

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[1] Received September 19, 1937.

droplets in the case of extremely lean but uniform mixtures. I also question that the excellent economy of the Diesel engine at part loads is caused by the fact that the fuel only is regulated; rather the economy at light loads is the economy inherent in the high compression ratio used with the Diesel, and at full load the good economy is really poor economy if based on what the cycle is capable of delivering providing all the fuel is burned early in the expansion stroke.

Our inability so far to provide means for efficiently burning a quantity of fuel corresponding to the full amount of oxygen available in the cylinder prevents us from obtaining the economy inherent in the high compression ratio of the Diesel engine, but recent researches show that the power output may very closely, if not actually, equal the power output of a spark-ignition engine. With a normally aspirated engine, as shown in figure 14 of the paper presented by Dr. Selden and myself, an indicated mean effective pressure of 163 lb. per square inch was obtained. This value corresponds to that obtained at a compression ratio of between 7.5 and 8.5 on a spark-ignition engine.

The authors' remarks on the slowness of fuel vapor diffusion are particularly important. It seems to me that this physical fact presents the chief obstacle to be overcome in the development of the high-speed Diesel. Also I agree with them fully in their statement that increased atomization will not necessarily improve engine performance. Their discussion on microstructure and macrostructure is particularly worth while However, I would sooner use the terms "atomization" and "vaporization" than "microstructure," and the term "distribution" rather than "macrostructure."

In the photographic researches on combustion conducted by the National Advisory Committee for Aeronautics we have never obtained any evidence of the high air velocities centrifuging the fuel to the outside of the chamber. Our researches indicate that it is extremely difficult to obtain a good mixture either by air flow alone or by nozzle design alone, but that the two means must supplement each other if the best performance is to be obtained. I also question the statement that greater flexibility is obtained with the use of air flow. We have idled an engine with a quiescent combustion chamber at 200 R.P.M. Our tests indicate that the difficulty in idling an engine without air flow can be overcome through the correct design of the injection system. Air flow definitely permits greater power output and lower fuel consumption to be obtained, particularly at high speeds.

In connection with the authors' statement that forced air movement may be much more intense than induced air movement, I would like to add that in our tests on the N. A. C. A. combustion apparatus we have found that the induced air movement obtained unintentionally may be

such as almost to destroy the forced air movement. Consequently particular care must be taken in the engine design so that the induced air movement will not oppose the forced air movement.

Our tests indicate that the penetration of the spray is probably less dependent on the atomization than on the closeness of the drops in the atomized jet. As was shown by Kuehn (Atomization of Liquid Fuels, Natl. Advisory Comm. Aeronaut. Tech. Mem. No. 331 (1935); translated from *Der Motorwagen*, December 10, 1934, January 20, 1935, Feb. 10, 1935), even the largest drops would not penetrate through the air in the combustion chamber more than a fraction of an inch unless they were sufficiently close to entrain the air within the spray.

It is questionable whether or not we should place so much emphasis on flame. Whether or not a flame nucleus is formed depends on our definition of flame. Webster's dictionary defines flame as "a body of burning gas or vapor." In their paper I presume that Mr. Boerlage and Mr. Broeze are referring to a luminous flame nucleus. If heat is being generated through the chemical reaction in the combustion chamber, the mixture is burning and we have combustion, even though we do not necessarily have luminous flame. In any case the luminosity is simply an indication of the temperature and constituents of the gas at the instant under consideration and has no direct relationship to the rate of pressure rise in the combustion chamber. In our own tests (A. M. Rothrock and C. D. Waldron: Natl. Advisory Comm. Aeronaut. Tech. Rept. No. 525 (1935)) we have recorded appreciable pressure rise before recording luminescence. But it must be further remembered that flame which is visible to the eye may or may not be recorded on the photographic film used in the tests, and that certain photographic films will record radiations that are not visible to the eye. Along this same line of discussion, the recent researches of Wilson and Rose (S. A. E. Journal **41**, 343-8 (1937)) offer additional information on the relationship between the start of radiation from the combustible mixture and the start of combustion pressure rise. When the motion pictures obtained by Rothrock and Waldron (see reference above) are projected they show various luminous combustion nuclei appearing and disappearing when the start of injection was 60° before top center. With the later injection starts, all the visible nucleii spread or merged into large combustion areas. I think a too detailed discussion of the process by which these nucleii are formed should wait until we have more information than is available at present.

The authors' statement that a mixture strength of 160 per cent of the theoretical autoignited at the lowest compression ratio is particularly interesting. This fact may have a direct bearing on the long after-burning period in the Diesel engine by requiring an overrich mixture in parts of the combustion chamber to initiate combustion.

FACTORS CONTROLLING DIESEL ENGINE PERFORMANCE

A. M. ROTHROCK and R. F. SELDEN

National Advisory Committee for Aeronautics, Langley Field, Virginia

INTRODUCTION

The performance of any internal-combustion engine, irrespective of its operating cycle, is primarily a function of the thermal energy liberated per cycle, the part of the cycle in which it is liberated, the compression ratio, and the mechanical limitations imposed by the engine structure. For the purpose of this paper, engine performance is determined by two quantities: first, the highest indicated mean effective pressure (i. m. e. p.) attainable, and second, the minimum fuel consumption expressed as pounds per indicated horsepower-hour. In order to secure optimum values for these quantities it is necessary that the combustion be completed as early in the power stroke as possible, with the provision that neither the explosion pressure nor the rate of pressure rise shall exceed certain limiting values.

The combustion in a compression-ignition or Diesel engine differs from that in a spark-ignition engine in that a large portion of the fuel must be mixed with air during the combustion period. The Diesel engine must be a compromise between extensive mixing before combustion, with its attendant early efficient burning but excessive rate of pressure rise, and limited mixing before combustion, giving a permissible rate of rise but a lower thermal efficiency. Provision must therefore be made for supplementary mixing of the major portion of the fuel charge with the available air after ignition by a proper coördination of the injection system, the combustion chamber, and directed air flow. It is the purpose of this paper to outline the influence of these factors on combustion in Diesel engines as revealed by a number of investigations conducted for the National Advisory Committee for Aeronautics (N. A. C. A.) on injection systems, combustion chamber design, and engine operating conditions, and to show how these factors control engine performance.

OPERATION OF TYPICAL INJECTION SYSTEMS

The fuel for most modern high-speed Diesel engines is injected, as a liquid under high pressure, through one or more small orifices directly into

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the combustion space of each cylinder by means of a displacement pump connected to an injection valve by a tube of appropriate dimensions. Each of the individual parts of such a system should be designed and coördinated to fulfill the following conditions: small variation in timing and fuel quantity from cycle to cycle; proper spray penetration and distribution for the particular combustion space; a sharp but controllable spray cut-off for various load conditions; and perhaps some control of injection rate and start of injection if the engine is intended to operate efficiently over a great speed range.

SINGLE - ORIFICE   NOZZLE

MULTIPLE - ORIFICE   NOZZLE

PINTLE   NOZZLE

IMPINGING - JETS   NOZZLE
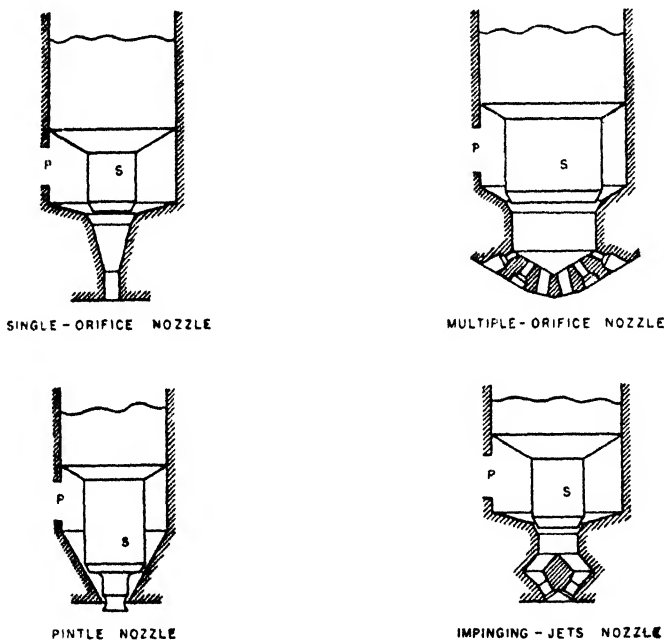
FIG. 1. Typical closed injection nozzles

The plain, pintle, multiple-orifice, and two-impinging-jets nozzles are representative of the many different nozzle styles used in commercial engines. Such nozzles are classified as open or closed, depending upon whether or not the cylinder gas has access after spray cut-off to an appreciable passage length above the flow-restricting orifice section of the nozzle. The nozzles sketched in figure 1 are all of the closed type with the valve stem S shown in the raised or injection position. If the oil pressure in the passage P falls sufficiently, a suitable spring above the valve stem forces the latter down until its seating surface is in contact with a corresponding

surface on the nozzle, thus providing a gas-tight seal between the cylinder interior and the fuel passage above the nozzle

The purpose of the nozzle is twofold,—to distribute the fuel throughout the combustion chamber and to assist in breaking up the fuel jet into the numerous droplets necessary for the intimate mixing of the fuel and air Disturbances of the fuel jet as it issues from the nozzle produce surface irregularities that are drawn out into fine ligaments by the relative motion of the fuel and air   The liquid in each ligament, after detachment from the main jet, quickly contracts into a spherical droplet by the action of surface tension   This process is illustrated in figure 2 for a low jet velocity

AT THE NOZZLE   3 INCHES FROM NOZZLE

5 INCHES FROM NOZZLE   10 INCHES FROM NOZZLE
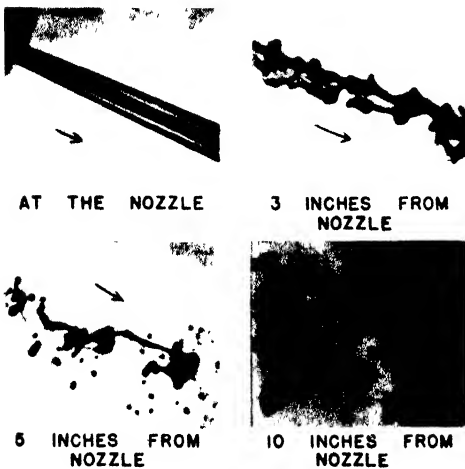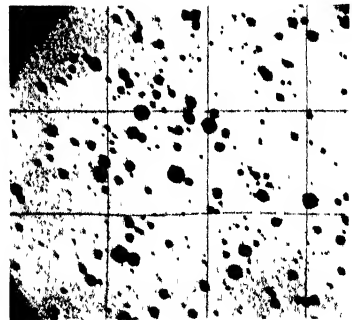
Fig 2

Fig 3

Fig 2 Disintegration of low-velocity jet in atmospheric air   Injection pressure = 100 lb per square inch

Fig 3   Fuel drop impressions in lampblack surface

(8)   Figure 3 is a photomicrograph of the impressions made by such drops after settling upon a lampblack surface (5)   A detailed analysis of the size distribution of these impressions corresponding to various injection pressures (or jet velocities) furnished the data for the curves in figure 4 The percentage of fuel in each group was based upon the volume corresponding to those drop impressions having diameters within 0 00025 in of the nominal or "mean" group diameter and the total volume for all such groups   It may be seen that for a given nozzle the average drop size decreases as the injection pressure increases, although the change is not very great at the higher jet velocities. Other conclusions drawn from these tests were as follows: Decreasing the orifice diameter results in more

uniform atomization of the spray and a smaller mean drop size   The density of the air into which the fuel is injected has little effect on the drop size distribution   Visual inspection of sprays cannot be used to estimate the relative drop size distribution
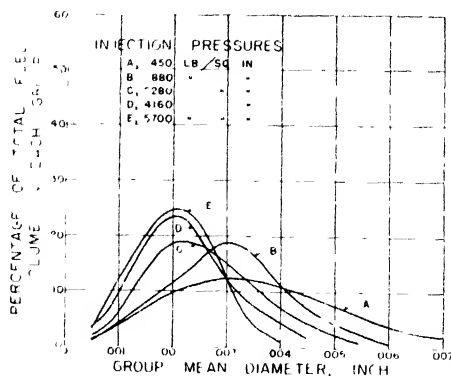
Fig 4 Effect of jet velocity on atomization

BROAD SIDE   NARROW SIDE
PLAIN   NOZZLE   TWO-IMPINGING-JETS NOZZLE
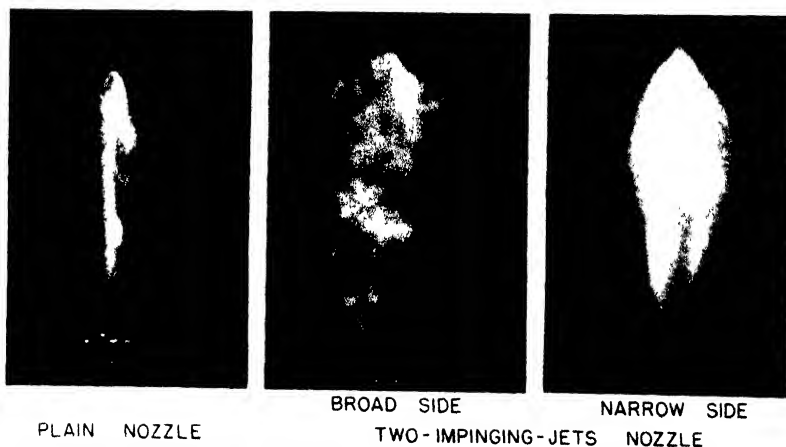
Fig 5 Spark photographs of sprays injected into atmospheric air

Spark photographs (6) of the symmetrical spray from a plain nozzle and of two views of the spray from a two-impinging-jets nozzle, each of which was injected into atmospheric air at a high jet velocity, are reproduced in figure 5   The multiple-orifice spray is simply a composite of plain sprays, whereas the pintle nozzle gives a spray of greater lateral spread   At gas densities greater than atmospheric the spray penetration decreases, as is illustrated in figure 6 for two plain nozzles and an im-

pinging-jets nozzle. The penetration into any gas is determined by the gas density rather than the gas pressure (4). For some applications the lower penetration of the impinging-jets nozzle may be advantageous, because of the greater lateral spread of the spray and the decreased impingement of the spray on the walls of the combustion chamber. Four such nozzles of the open type are used per cylinder in the Junkers aircraft Diesel. The length–diameter ratio of round-hole orifices giving the best spray penetration lies between 4 and 6, whereas the greatest lateral spread, or spray angle, occurs with ratios between 2 and 3 (3). It is for this reason that the smaller orifices are shown countersunk in the multiple-orifice nozzle in figure 1.

Further information as to the relative spatial distribution of fuel in sprays from various nozzle types has been obtained (7) by determining the
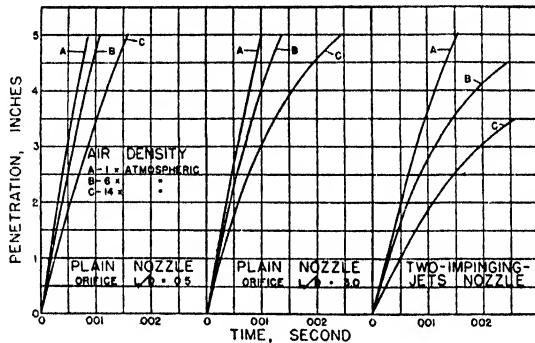
Fig 6. Effect of air density on penetration of spray tip. Injection pressure = 4000 lb. per square inch.

quantity of fuel caught by suitable receiving apparatus set up in front of the nozzle for a definite number of injections into air of the desired density. Typical curves for the distribution obtained with three of the nozzle types shown in figure 1 are given in figure 7 for an air density fourteen times that of atmospheric air. The impinging-jets nozzle gave the best distribution within the spray, the pintle nozzle was intermediate, and the plain nozzle gave the poorest distribution. For plain round-hole orifice nozzles some improvement in lateral distribution within the spray resulted from an increase in injection pressure, the improvement being a function of orifice size. Low viscosity fuels also gave better distribution. The curves illustrate the difficulty of finding a satisfactory combination of orifice and combustion chamber design and the necessity of employing air movement within the combustion chamber to assist in the mixing of fuel and air. At present, the pintle nozzle is widely used in commercial
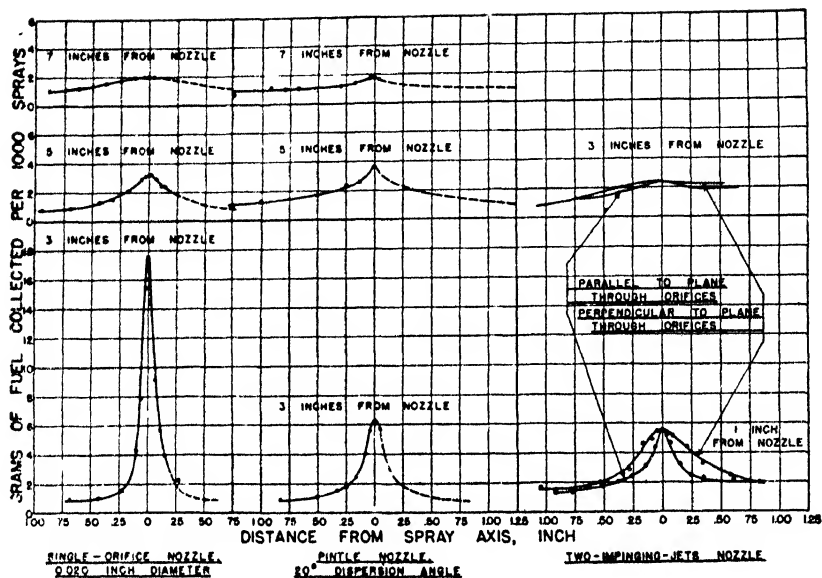
FIG. 7. Distribution of fuel within sprays
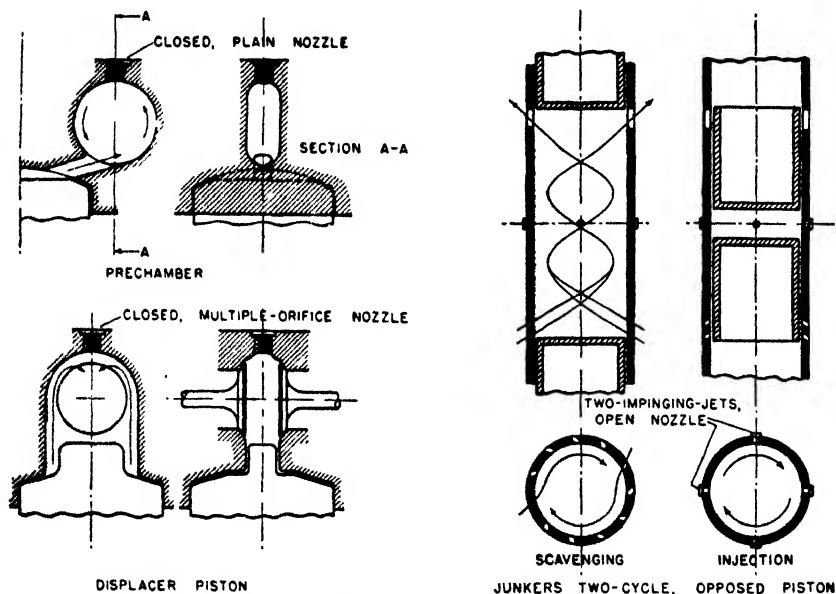
FIG. 8. Typical combustion chambers for inducing air flow

applications employing some form of precombustion chamber, but the multiorifice nozzle has been found most effective in tests at this laboratory with integral types of combustion chambers

COMBUSTION AND COMBUSTION CHAMBER DESIGN

If it were not for the fact that available injection systems are incapable of distributing the fuel in a completely satisfactory manner, there would be little excuse for the varied combustion chamber designs that have been used in commercial Diesel engines. All such designs have as their basic purpose one or both of two aims (1) to furnish supplementary fuel-air mixing to correct partially for the deficiency in the spray distribution and (2) to diminish the combustion shock or Diesel knock. As fuels of sufficiently high ignition quality are available, the problem of securing adequate mixing is distinctly of greatest importance, particularly with high-speed engines. On this basis the combustion chamber should possess two characteristics first, it should have a shape conducive to the best distribution of the fuel with respect to the air charge and second, it should contribute as far as possible, by induced air flow and turbulence, to the secondary mixing of unburned or incompletely burned fuel with unused oxygen. Obviously an optimum coordination of injection system and combustion chamber shape minimizes the required auxiliary mixing by air flow and turbulence. For this reason high dispersion or multiple-orifice nozzles generally give better results.

Three typical systems for obtaining air flow in the combustion space are illustrated diagrammatically in figure 8, each of these being at present an optimum design for its type. The air flow is induced by the restricted connecting passage between two portions of the combustion space in the prechamber type (9), and by the restriction between the combustion chamber and displacement volume during the latter part of the compression stroke in the displacer-piston type (10, 11, 13). In the Junkers two-cycle design the flow is generated by directed intake ports or baffles. It is particularly important to note that each design is basically a disk chamber in which is induced a directed flow of the air charge. The displacer-piston type is really an adaptation of the so-called quiescent-chamber engine without any projection on the piston as developed by the National Advisory Committee for Aeronautics over a period of years (2)

The fuel must not only be atomized and distributed throughout the air in the combustion chamber, but it must also be vaporized through absorption of heat from the air so as to form a combustible mixture. The rapidity with which the injected fuel absorbs heat from the surrounding air is indicated by figure 9 (23). The upper record shows the decrease in total gas pressure attending the heat transferred to Diesel fuel upon its

injection into heated and compressed nitrogen   This decrease began
with the very first portion of the fuel injected   The lower record cor-
responds to the third injection into the same air charge after reestablish-
ment of thermal equilibrium following the first two injections   The
decrease in the initial rate of pressure drop (or heat transfer) evident in
the lower record must be attributed to one or both of the following   the
greater heat capacity of the air vapor mixture existing after the second
injection, or an inhibition of the vaporization of a portion of the fuel,
which presumably occurred in the absence of vapor

An indication of the rapidity of the vaporization process in an engine is
furnished by the high-speed motion pictures reproduced in figure 10 (16)
The photographs in each series were obtained by means of suitably timed
spark   and show a silhouette of a quiescent combustion chamber provided
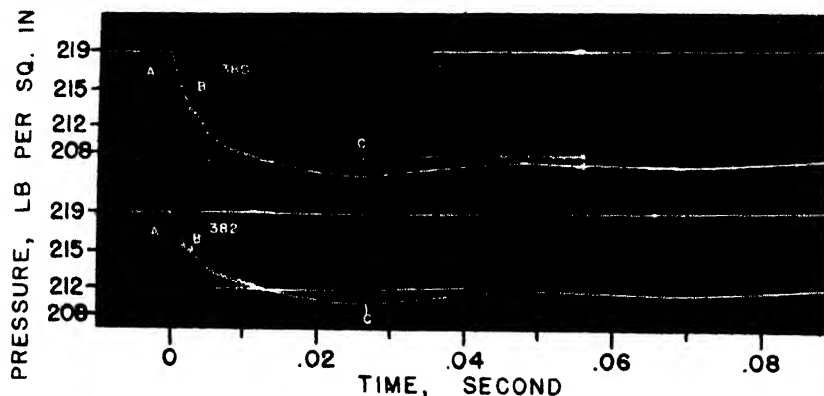
Fig 9 Effect of fuel vapor concentration on rate of heat transfer

with front and rear windows 2 5 m m diameter   In taking the photo-
graphs, the engine was motored over and a single charge of fuel injected
into the combustion chamber   Combustion was prevented by the ex-
tremely low temperature at which the engine was operating   Each series
of photographs corresponds to a fuel having a dew point markedly differ-
ent from that of the others, the injection advance angle being maintained
constant   The chamber contents became more transparent as the spray
core disappeared through its vaporization and its movement beyond the
field of view   On the expansion stroke the contents of the chamber sud-
denly became opaque, as a result of the condensation of the vapors.   The
order of condensation in terms of crank angle was the same as that for the
volatility or dew points of the fuels   The fact that the fuels were vapor-
izing was confirmed by the results of further tests in which the injection

advance angle, the fuel quantity, the engine speed, and the engine temperature were varied independently

The extent to which the fuel is mixed with the air in the combustion chamber can be studied by investigating the efficiency of the combustion and the efficiency with which the heat energy extracted from the fuel is transformed into useful work. By combustion efficiency is meant the fraction of available heat energy that is extracted from the fuel during the latter part of the compression stroke and during the power stroke. The efficiency with which this extracted heat energy is transformed into indicated work is termed the cycle efficiency. Although these two efficiencies are independent of each other, they are generally studied together. The
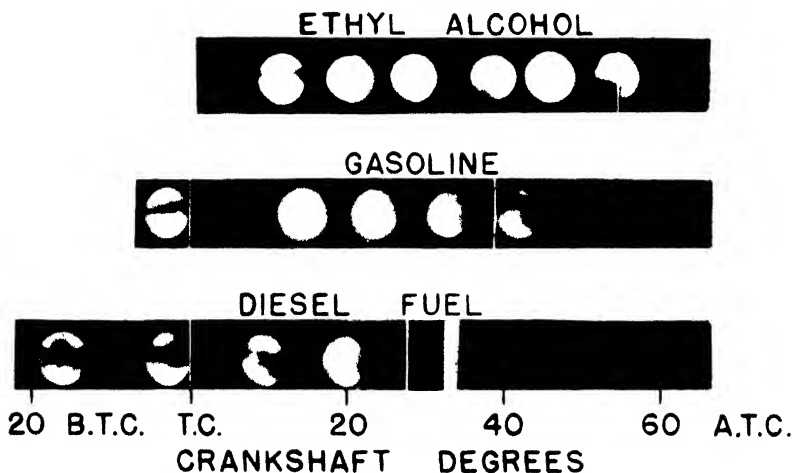
Fig 10 Vaporization and condensation of fuel Engine R P M = 1500; I A A = 20°

product of these two efficiencies is the indicated thermal efficiency of the engine and is the factor of primary interest.

The extent to which the fuel is burned is indicated to a certain degree by high-speed motion pictures of the combustion process and to a greater degree by an analysis of the indicator cards taken during engine operation. High-speed motion pictures were taken on the same single-cylinder quiescent-chamber test engine, operating under its own power for a single cycle, as was used for the vaporization work. In these tests the effects of high wall temperatures and of exhaust gas dilution were not present; otherwise, the test conditions meet very closely those experienced in actual engines. The quiescent chamber provided a minimum of air movement so that the distribution and dispersion of the fuel by the injection nozzle could be
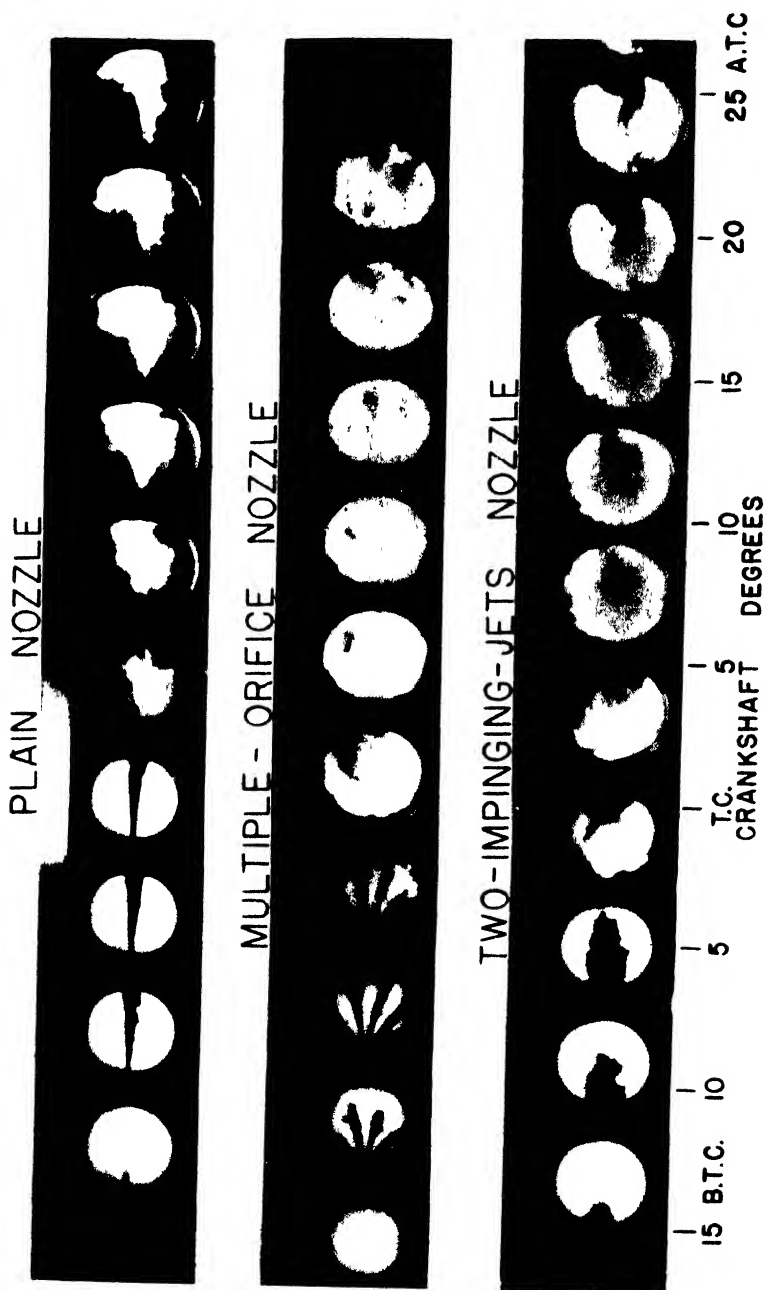
Fig. 11 Variation of fuel distribution and flame formation with nozzle design Engine R P M = 1500, I A A = 15°

studied. Photographs of the injection and combustion of the fuel taken under this condition at a rate of about 2000 frames a second are presented in figure 11 (19) The figure emphasizes the inadequacy of the fuel dispersion and distribution from a single round-hole orifice, and the improvement that is obtained from the multiorifice nozzle With the single round-hole orifice the area reached by the flame indicates the area of the fuel dispersion Although there is continual vaporizing of the fuel sprays, the spray core and at least part of the envelope are visible in every case up to the start of combustion Much of the combustion chamber is never reached by the burning gases With the six-orifice nozzle the flame not only reaches all the visible portion of the combustion chamber, but persists for an appreciable time interval. The fact that ignition often occurred between the sprays is of interest. The slit nozzle, although giving fairly uniform distribution throughout the spray, did not disperse the fuel throughout the chamber, so that the mixing was inferior to that given with the six-orifice nozzle, even though the latter contained the six dense spray cores The dense core is apparently necessary to obtain sufficient spray penetration in a combustion chamber which does not have high-velocity air flow

The effect of air flow on spray development and on combustion is shown in the three series of schlieren, high-speed, motion-picture photographs, together with the respective combustion chamber arrangements, as in figure 12 (20) Except for the definite deflection of the opaque fuel in the two lower series, these pictures do not convey the impression of air motion nearly so well as the projected motion pictures Other than for the schlieren feature, the upper series of photographs is similar to that in figure 11 As the displacer on the piston, as shown opposite the second series, entered the combustion chamber a violent swirl of the air as a whole was produced in the chamber Even though the spray core itself was not destroyed by the air swirl, a greater combustion chamber area was reached by the flame than was the case without the air movement With the multiorifice nozzle and the two-passage displacer the pictures indicate some air movement, but a comparison with similar pictures taken without air flow shows that there was no apparent improvement in the mixing of the fuel and air Nevertheless, both the single and double passage displacers showed a decided improvement in performance for a combustion chamber of similar design on a single-cylinder test engine Apparently with a nozzle that distributes the fuel reasonably well, the chief function of the air flow is not to disrupt completely the spray cores, but to improve the mixing between the individual sprays. In fact, it seems that the sprays contribute to the destruction of the air movement, but in so doing the desired mixing of the air and fuel is partially achieved.
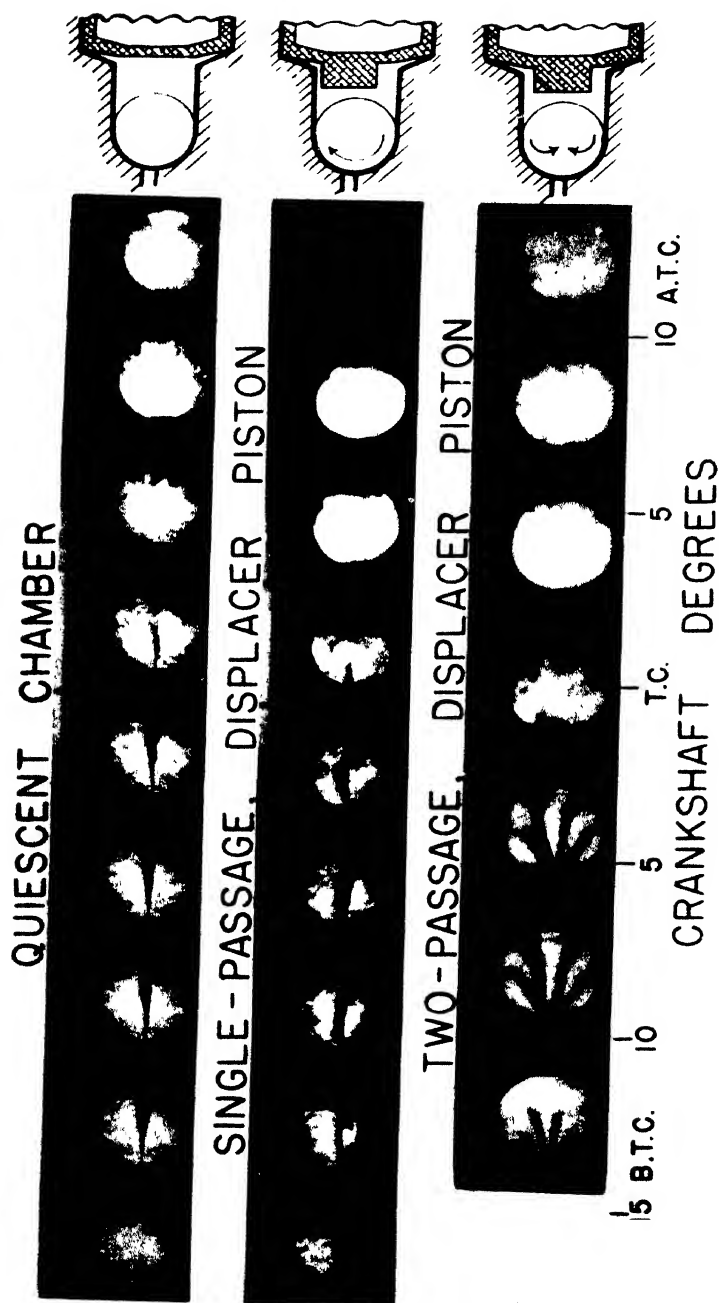
FIG 12 Effect of air flow on fuel sprays   Engine R P M = 1500; I A A = 15° to 20°

By an adaptation of a method developed by Schweitzer (21) for the analysis of engine indicator cards not only the combustion efficiency but also the cycle efficiency can be obtained to a fair degree of accuracy. The curves in figure 13 show the effect of fuel-injection advance angle (I. A. A.) on the indicator card and on the rate of combustion in the quiescent combustion chamber (14). The corresponding combustion and cycle efficiencies were computed from the indicator cards shown and the known fuel quantity injected. These efficiencies are given in table 1.

The data show that the ignition lag remained practically constant for the different conditions. Therefore it seems reasonable to believe that a
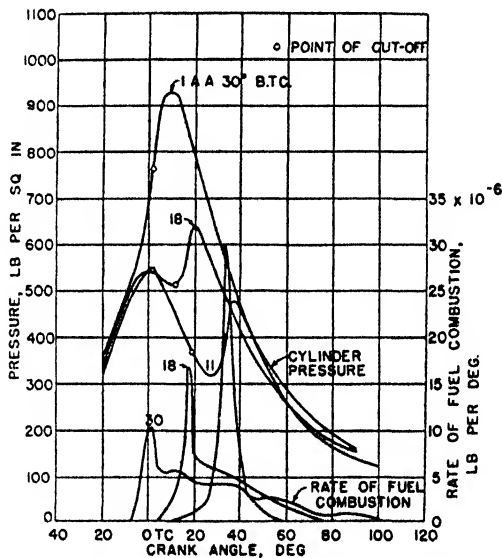
Fig. 13. Effect of injection advance angle on combustion rates

factor equally important with the ignition lag is the time interval between spray cut-off and the start of rapid combustion. Spray photographic tests have shown that only after spray cut-off does the spray core disintegrate. A comparison of figure 13 and table 1 shows that as the maximum rate of combustion was increased, the combustion efficiency also increased, but that the cycle efficiency decreased because of the lateness of the burning. As a result the thermal efficiency was highest for the earliest I. A. A. Had the tests been run on different fuels instead of different injection advance angles, then the fuel giving the highest combustion efficiency would also have given the highest thermal efficiency. This same affect has been obtained by using the same fuel and injection advance

angle, but operating the engine at different jacket temperatures (2). In these tests an increase in the jacket temperature decreased the ignition lag, but also decreased the combustion efficiency because of the shorter lag.   These data have led to the conclusion that the Diesel engine should be operated on the lowest cetane number fuel consistent with easy starting and permissible rates of pressure rise.

Figure 13 also shows the long after-burning period that exists in most high-speed Diesel engines.   Until means are derived for burning this fuel earlier in the expansion stroke, the cycle efficiencies inherent in the high expansion ratio of the Diesel engine will not be realized.   In fact, the elimination of this after-burning period will probably do more to advance the Diesel engine than any other single factor.   In other tests conducted by the National Advisory Committee for Aeronautics (1, 15, 17) it has been shown that if the lag between cut-off of injection and start of combustion pressure rise is too great, the combustion efficiency and the combustion rates decrease.   It appears, therefore, that there is a certain value

TABLE 1

Fuel-injection advance angle and efficiency

I. A. A	FUEL–AIR RATIO	COMBUSTION EFFICIENCY	CYCLE EFFICIENCY	THERMAL EFFICIENCY
30	0 039	0 59	0 57	0.33
18	0 046	0 64	0 46	0 30
11	0 051	0 69	0 36	0 25

of this lag which gives a maximum combustion efficiency and rate-of-pressure rise   For this reason, if the after-burning period can be eliminated, not only the cycle efficiency but perhaps the combustion efficiency as well will be increased.

The after-burning is probably caused by inadequate mixing of the fuel and air.   This mixing is controlled by the form of the fuel spray, the degree of atomization, the rate of fuel vaporization, the rate of vapor diffusion, and the degree and form of air movement within the combustion chamber. It is questionable whether any improvement in atomization over that obtained at present will further improve the distribution of the fuel.   Tests were conducted at the laboratories of the National Advisory Committee for Aeronautics, in which a high-velocity air jet was directed through the injection nozzle with the fuel spray.   Although atomization and burning tests showed the fuel to be much better atomized, the system did not give any improvement in engine performance.   The rate of fuel vaporization is apparently comparatively high (16), and the test results indicate that, with the fuels used on commercial engines, the vaporization is sufficiently

fast in every case to provide good mixing of the fuel and air.   The diffusion of the fuel vapors appears to be too slow to provide adequate mixing even though nozzles with good distribution characteristics are employed (18, 19).   It can be concluded that the improvements in mixing must be obtained through close coördination of the spray form and the air flow in the combustion chamber.

It is evident from the solid curves in figure 14 that the indicated mean effective pressure and the specific fuel consumption improve with N. A. C. A chamber design in the following order: quiescent chamber, prechamber, and quiescent chamber in combination with a displacer piston (2, 9, 11). The dashed curves show that the response to boosting[1] measured in terms of the increase in indicated mean effective pressure is about the same at
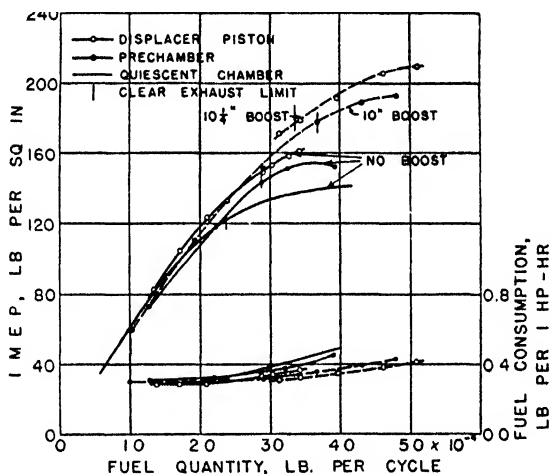
FIG. 14. Performance with typical combustion chambers

1500 R.P.M. for the prechamber and displacer engines.   The clear exhaust limit for the quiescent chamber occurs at a considerably lower fuel quantity than for the unboosted prechamber and displacer engines.   Considered on the basis of the limiting indicated mean effective pressure with clear exhaust, the displacer piston possesses an advantage, either boosted or unboosted.

The displacer-piston tests have been extended to 2500 R.P.M. and a boost of 20 in. of mercury, the resulting fuel consumption and maximum indicated mean effective pressure for a clear exhaust being 0.34 lb. per indicated horsepower-hour and 235 lb. per square inch, respectively, at a

[1] The boost data presented in this paper have not been corrected for supercharger power.

maximum cylinder pressure of 1200 lb. per square inch (12).   These high performance figures at 2500 R.P.M. result from a combination of one or more of the following factors: greater permissible maximum cylinder pressure, improved cylinder scavenging with inlet and exhaust valve overlap, and better response to boosting.

The improvement in thermal efficiency with boosting, as shown by the decrease in specific fuel consumption at the higher loads, is another notable feature shown by figure 14.   This same tendency is again evident in figure 15 (22).   In this figure the ratio of the absolute explosion pressure 0.004 sec. after ignition to the initial pressure is plotted against the ignition lags obtained when the fuel charge is injected into a constant-volume bomb containing air at several respective temperatures and densities.
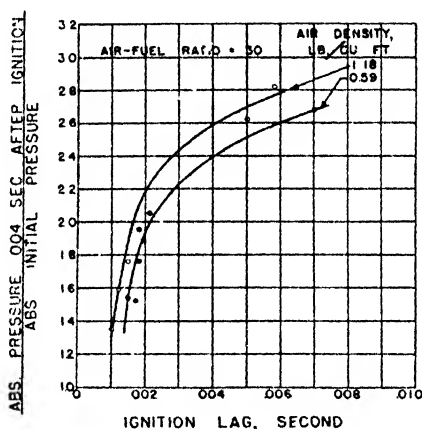
FIG. 15. Improvement in combustion with increasing air density

The lower density approximates those existing in a Diesel engine at normal injection advance angles, whereas the higher density corresponds to that in an engine at top center operated with a boost of about 10 in. of mercury.   The improvement in combustion efficiency with increasing density is appreciable, particularly for the shorter ignition lags such as are permissible in engines.

CONCLUSION

From the data obtained on the high-speed Diesel engine at the laboratories of the National Advisory Committee for Aeronautics and at various other research institutions it is possible to draw certain definite conclusions and to outline the direction in which experimentation should go.   One important conclusion is that the flat-disk combustion chamber

offers the greatest promise. In the researches reported here, it was found that the flat-disk chamber gave the best performance with either the pre-combustion or the direct-injection chamber. In the precombustion chamber it was found that the best performance was obtained with most of the volume in the precombustion chamber of the flat-disk form. The outstanding performance obtained in Germany on the Junkers engine is also obtained with the flat-disk chamber. The chief difference between the three engines is in the nozzles used for the injection of fuel, the displacer-piston engine using a multiorifice nozzle, the precombustion chamber engine a single round-hole orifice nozzle, and the Junkers engine four impinging-jets nozzles. In each case the choice of nozzles has been the outcome of considerable experimentation and represents the best com-bination of combustion chamber design, air swirl, and nozzle design ob-tained so far. All three combustion chambers use a high-velocity air swirl, although the method of producing the swirl differs. The pre-combustion chamber engine has the disadvantage of an unscavenged space, which definitely limits its performance to a value below that of the other two types. More research is necessary on the effects of the design of the nozzle for the injection of fuel to determine, if possible, an optimum form of nozzle.

More data are necessary on the fuel distribution within the combustion chamber. There is little quantitative information on the distribution throughout the combustion chamber from the start of injection to the completion of the first 30 degrees of the expansion stroke. Finding the air–fuel ratio in different parts of the chamber during this time interval presents a difficult problem, but efforts to find it should be made. Tests should be conducted to determine whether the after-burning period is caused by inadequate mixing or by certain chemical phenomena. If it is chemical, it is possible that the use of certain fuel dopes will help to speed up the late burning.

Although it has not been brought out in this paper, there is a need of data on the effect of the rate of injection on the combustion efficiency. It is probable that to obtain widely different rates with adequate nozzle distribution, it will be necessary to use a unit injector. The unit injector, in which the piston of the injection pump is mounted as closely as possible to the injection nozzle, shortens the comparatively long time interval for pressure changes to be transmitted throughout the injection system.

The question of fuel rating, which is proving so bothersome in the gasoline engine field, appears to be fairly straightforward for Diesel engines. There are at least two methods of Diesel fuel rating, either of which is satisfactory, namely, the ignition lag as measured in the engine or the ignition lag as measured in a bomb at temperatures and densities equivalent to those in the engine.

As the speed of the Diesel engine is increased there is going to be a need for even closer coördination of the injection system and combustion chamber design. In addition, the injection system will need further development in order to inject the fuel in the shortened permissible time. Here again, it is probable that the unit injector will be at an advantage over the systems in general use at present, in which there is an injection tube of appreciable length between the injection pump and the injection valve.

REFERENCES

(1) COHN, M , AND SPENCER, R. C : Natl Advisory Comm Aeronaut., Rept. 544 (1935).

(2) FOSTER, H H : Natl Advisory Comm Aeronaut , Rept. 568 (1936)

(3) GELALLES, A. G.. Natl Advisory Comm Aeronaut , Rept 402 (1931).

(4) JOACHIM, W F., AND BEARDSLEY, E G : Natl Advisory Comm Aeronaut , Rept 281 (1927).

(5) LEE, D W : Natl Advisory Comm Aeronaut , Rept 425 (1932)

(6) LEE, D W : Natl. Advisory Comm Aeronaut , Rept. 520 (1935).

(7) LEE, D. W · Natl Advisory Comm Aeronaut , Rept. 565 (1936)

(8) LEE, D W , AND SPENCER, R C : Natl. Advisory Comm. Aeronaut., Rept. 454 (1933)

(9) MOORE, C. S., AND COLLINS, J H , JR : Natl. Advisory Comm. Aeronaut., Rept. 577 (1937)

(10) MOORE, C. S., AND FOSTER, H. H.: Natl Advisory Comm. Aeronaut., Note 518 (1935)

(11) MOORE, C. S., AND FOSTER, H. H : Natl. Advisory Comm. Aeronaut , Note 569 (1936)

(12) MOORE, C S., AND FOSTER, H. H : Natl. Advisory Comm. Aeronaut., unpublished report

(13) MOORE, C. S., AND COLLINS, J. H., JR : S A E. Journal 40, 263 (1937)

(14) ROTHROCK, A. M : Natl Advisory Comm. Aeronaut., Rept 401 (1931).

(15) ROTHROCK, A. M , AND COHN, M : Natl. Advisory Comm. Aeronaut., Rept. 512 (1934)

(16) ROTHROCK, A. M., AND WALDRON, C D : Natl. Advisory Comm. Aeronaut., Rept. 435 (1932).

(17) ROTHROCK, A. M , AND WALDRON, C. D.: Natl. Advisory Comm. Aeronaut., Rept. 525 (1935).

(18) ROTHROCK, A. M., AND WALDRON, C. D.: Natl. Advisory Comm. Aeronaut., Rept 545 (1935).

(19) ROTHROCK, A. M , AND WALDRON, C. D.: Natl. Advisory Comm. Aeronaut., Rept. 561 (1936)

(20) ROTHROCK, A. M., AND WALDRON, C. D.: Natl. Advisory Comm. Aeronaut , Rept 588 (1937)

(21) SCHWEITZER, P. H : Penn. State Coll. Eng. Expt. Sta., Bull. No. 35 (1926).

(22) SELDEN, R. F.: Natl Advisory Comm Aeronaut., Rept. 617 (1938).

(23) SELDEN, R. F , AND SPENCER, R. C.: Natl. Advisory Comm. Aeronaut., Rept. 580 (1937).

METHODS OF RATING DIESEL FUELS

P. H. SCHWEITZER

School of Engineering, The Pennsylvania State College, State College, Pennsylvania

I. MECHANISM OF THE DIESEL COMBUSTION KNOCK

The Diesel process is frequently described as injecting liquid fuel into highly heated air, the fuel igniting instantly upon its entrance into the cylinder. If this description were accurate, there would be no combustion knock in Diesel engines, generally speaking. The introduction of the fuel into the cylinder is a gradual process, if for no other than mechanical reasons. The injection extends over a period of 20 to 35 crank degrees, sometimes more, seldom less. During this period the introduction of the fuel is more or less uniform. If the ignition were instantaneous, the rate of pressure rise would follow the rate of injection and be moderate. Combustion knock, on the other hand, always is accompanied by a very rapid pressure rise.

However, the process described is upset by the ignition lag. The fuel injected does not ignite instantaneously. The significance of the delay period is discussed in another paper (9) of this symposium. For us it will suffice to say that the longer the delay the more violent the subsequent ignition and the more severe the combustion knock.

Almost every factor that causes a spark-ignition engine to knock makes the compression-ignition engine run more smoothly (45). In both cases the knock is caused by the autoignition of a considerable portion of the charge, but while in a spark-ignition engine it is ordinarily the last portion of the charge which autoignites, in the compression-ignition engine combustion is initiated by autoignition. This explains the different behavior of the two types of engines.

Consequently fuels of paraffinic base, consisting mostly of saturated straight-chain hydrocarbons, are the smoothest and most desirable fuels for Diesel engines, while cracked fuels and also straight-run aromatics burn roughly, benzene being about the worst of all. Gasoline antiknocks have the reverse effect in Diesels (37), while proknocks, consisting mostly of mild detonants like ethyl nitrate, added even in a small percentage reduce the Diesel knock remarkably. This is explained by the fact that paraffin fuels and ethyl nitrate ignite after a comparatively short delay and

do not permit the accumulation of a considerable amount of combustible charge in the cylinder

II. HISTORY OF DIESEL FUEL TESTING

Rieppel (43), in 1907, as one of the earliest research workers on the behavior of liquid fuels in compression-ignition engines, recognized that no relation existed between the flash point or burning point of a fuel and its ability to ignite spontaneously inside an engine cylinder.

Holm (23), in 1913, investigated autoignition temperatures in oxygen by allowing oil globules to drop to a porcelain crucible cover heated inside a vertical tube furnace swept through by a stream of oxygen.

Constam and Schlaepfer (13) continued the investigation with increased accuracy, but they could not share Holm's opinion that the spontaneous ignition temperature was of decisive influence on the suitability of fuel oils for Diesel engines.

A simple and successful autoignition temperature tester operating with air under atmospheric pressure was developed by Moore (36) in 1919, which has been perfected by Wollers and Ehmcke in the Krupp laboratories (51). In Jentsch's modification of the open crucible, the oxygen feed is closely controlled.

Compressed air in a bomb was used by Tausz and Schulte (50) and atomization of the fuel added by Hawkes (16), Neumann (39), Foord (15), Holfelder (22), and Michailovra (33). These investigations have shown that self-ignition temperature depends to an enormous degree on the delay period and to an appreciable degree on the air pressure, density, air–fuel ratio, material of the crucible, and atomization of the fuel. By agitating the air in the bomb Neumann (39) obtained self-ignition temperatures that were much higher than those for stagnant air, except for very short ignition lags, when the reverse was true.

The above investigations rated Diesel fuels in somewhat similar order and have shown that paraffinic fuels have lower self-ignition temperatures than aromatic or naphthenic fuels. But the order of magnitude of the time lag in simple bomb tests was a multiple of 1/10 second, compared to a few thousandths of a second obtained in compression-ignition engines. In recently constructed bombs, however, using high pressure, turbulence, and fuel atomization, ignition lags were measured (33) that are comparable with those obtained in engines.

In 1923 Hesselman (18) described a method for measuring ignition lag, which he used on his engine. In 1931 Le Mesurier and Stansfield (29) gave results of tests to determine the difference in behavior of a wide range of fuels in several compression-ignition engines, and showed that, in any given engine, the combustion knock was broadly related to the delay which occurred between the moment of injection and the beginning of rapid

pressure rise, which they measured essentially in the same way as Hesselman. Different engines seemed to have only slightly different relative effects on the fuels tested.

In the same year Boerlage and Broeze (6) published their results on an engine-test method of rating Diesel fuels. The tests were made in a relatively slow speed engine by the throttling method, and each fuel was rated in terms of the blend of cetene and mesitylene which matched it in ignition lag. The tests have shown surprisingly good correlations, indicating not only that the method is dependable but also that differences between engines and running conditions were of relatively slight effect upon the rating.

In January, 1932, Pope and Murdock (40) reported on their tests made with a modified C.F.R. knock-testing engine. In these tests the engine was of the variable compression type, and the rating was based on the lowest compression ratio at which the samples of fuel would just ignite under controlled temperature conditions. While running the engine under such borderline conditions did not prove practical, with a "motored engine" the critical compression ratio method gave very useful results.

In July, 1932, Boerlage and Broeze (7) proposed that ratings in ignition quality be made in terms of "cetene numbers", using cetene and alpha-methylnaphthalene as primary standard. In 1935 the A.S.T.M. (1) replaced cetene in this country by cetane for a standard reference fuel of high ignition quality.

Until recently ignition lag determinations were made from indicator diagrams. In 1932 Boerlage and Broeze (7) described an inertia lag meter, and a year later (8) reported cetene ratings performed with a modified Midgley type bouncing pin. The "knockmeter delay method" which has been most widely used in this country is an outgrowth of this method, and was developed by T. B. Rendel (41) in coöperation with the Waukesha Motor Company, the builders of the converted C.F.R. engine which has been tentatively adopted for Diesel fuel rating.

In 1933 Schweitzer, Dickinson, and Reed (46) proposed the use of a predetermined ignition lag, to be obtained by a corresponding adjustment of the compression ratio, for rating. In 1935 Hetzel and Schweitzer (20) replaced the bouncing pin by a magnetic pick-up, which flashed the neon lamp of a protractor through an electronic relay.

One of the first empirical equations based on physicochemical data, and indicative of the ignition quality of the fuel, was proposed in 1931 by Butler (11) and called "Ignition index:"

$$\text{Ignition index} = (1 - \text{specific gravity}) \frac{\text{specific gravity}}{\text{dispersion}}$$

$$\times \text{ average boiling point (°F.)}$$

The specific gravity and dispersion are to be taken at 100°F. This was superseded in 1934 by the Diesel index of Becker and Fischer (4),—a formula involving gravity and aniline point which has subsequently become rather popular

In the same year Moore and Kaye (35) proposed the viscosity–gravity number, which has been modified by Hill and Coates (21); this formula contains only viscosity and gravity.

One year later Jackson (26) proposed the boiling point–gravity number, which uses the 50 per cent distillation point and gravity in a formula.

In 1935 Heinze (17) proposed as an index the parachor of Sugden (49), $p = S^{\frac{1}{4}}/D$, where S = surface tension and D = specific gravity. When p is plotted against the molecular weight, characteristic straight lines are obtained, one for each class of hydrocarbons, which correlates well with the cetane rating.

The U.O.P. (Universal Oil Products) characterization factor, proposed by Hubner and Murphy (25) in 1935, includes the same factors as the boiling point–gravity number in a different combination.

As a further refinement in 1937 Hubner (24) introduced the ignition quality number, which is obtained by multiplying the Diesel index by the 50 per cent distillation point.

Marder and Schneider's (32) formula based on the boiling point index and Kreulen's (28) "ring analysis" are the most recent contributions along this line.

III. SCALE FOR EXPRESSING RATING

No matter what testing method is adopted for measuring ignition quality, it is essential to determine the manner in which the rating of the fuel shall be expressed. This problem is only loosely related to the method of rating. Using the engine rating, one way to express the rating would be to use the measured factor for scale, as the ignition lag in degrees, the lowest usable compression ratio, the required compression ratio to produce a predetermined ignition lag, the maximum rate of pressure rise, and others.

Another way to express the rating is based on two standard reference fuels, one of high and the other of low ignition quality. The test fuel is matched with a blend of the two reference fuels mixed in such proportion that its ignition quality (in the arbitrary scale of the test) is equal to that of the reference blend. The rating of the fuel is then expressed as the percentage concentration of the reference fuel of high quality.

This second method can be used with any testing method that may be adopted,—bomb, physicochemical, or engine tests,—and it offers certain distinct advantages. Rating expressed in a reference fuel scale is no doubt less affected by the instrument factors. But the deciding consideration

in the adoption of the cetene (later cetane) scale was the preceding experience with gasoline knock rating. In the early period that was expressed by Ricardo's H.U.C.R. (highest useful compression ratio), but that gave way first to the toluene equivalent and later to the octane number. Technologists accustomed to the octane number were quick to adopt the cetene number when it was proposed by Boerlage and Broeze.

The selection of the reference fuels required, however, a careful study. For reproducibility they should be pure substances of a known chemical composition, which are stable in storage. For range they should possess higher and lower ignition quality, respectively, than any fuel to be tested. For validity they should possess a chemical constitution and physical

TABLE 1

Properties of cetane and alpha-methylnaphthalene

PROPERTIES	CETANE*	ALPHA-METHYL-NAPHTHALENE†
Specific gravity 60/60 °F	0 778	1 018
Flash point, closed cup, °F	230+	214
Pour point, °F	+65	+50
Viscosity, SSU at 100°F	38	37
Distillation range, °F.		
Initial boiling point	516	450
10 per cent	532	456
50 per cent	534	438
90 per cent	536	460
End point	543	482
Aniline point, °F	204.0	Miscible

* As supplied by E. I du Pont de Nemours and Company.

† As supplied by Reilly Tar and Chemical Company.

properties (viscosity and volatility) not much different from those of the normal fuels. Finally, they should be available at a reasonable price.

The reference fuels which were adopted by the A.S.T.M. as most satisfying these requirements are cetane, $C_{16}H_{34}$, and alpha-methylnaphthalene, $C_{11}H_{10}$. The properties of these substances are given in table 1.

Table 1 shows that the properties of these hydrocarbons are in line with those petroleum fuels which are used most in high-speed compression-ignition engines. The ignition quality of cetane is about equal to that of cetene, $C_{16}H_{32}$, but it is claimed that it is more stable in storage.

Since June, 1935, when the A.S.T.M. recommended its use, the cetane scale has become practically universal in this country as a measure of ignition quality. In Europe the use of the cetene number scale has been continued to date.

IV. THREE GROUPS OF TEST METHODS

A. Bomb tests

The primary objective with the crucible and bomb tests was to determine the self-ignition temperature of the fuel. It has been observed that fuels of high self-ignition temperature either fail to ignite at all in the engine, or if they do ignite there is a long delay with a corresponding combustion knock. So self-ignition temperature was taken for a measure of ignition quality. The Moore apparatus uses an open porcelain crucible heated in a furnace or solder bath into which drops of oil are admitted while the temperature of the crucible is raised by small increments until the fuel autoignites. This method was simple and well adapted to laboratory practice. It was found (29, 6, 5, 4), however, that the self-ignition temperatures obtained with such an apparatus lie too close together and, furthermore, they do not rate fuels in the same order as their engine behavior. This should not surprise us, if we realize that temperature is just one of the many factors that determine autoignition. Others are chamber pressure, air motion, fuel drop size, fuel-air ratio, and time lag of ignition. Bridgeman and Marvin (10) have shown that even the size and material of the crucible influenced the self-ignition temperature.

Subsequent efforts have been directed at creating conditions in an ignition bomb similar to those in the engine, and improved ignition testers have been evolved. Such recent variants as Holfelder's (22) and Michailovra's (33) inject finely atomized sprays into heated dense air, agitated to simulate turbulence, and measure the delay of the ignition. The results obtained are comparable to and correlate well with engine tests. By the time the bomb has reached this perfection it has become so complicated that it now offers no advantage either in first cost or in ease of operation over the test engine.

The ideal that self-ignition temperature as a characteristic property of the fuel would determine its ignition behavior did not materialize. Whether or not a fuel drop ignites at a certain temperature depends a great deal on how long the drop is exposed to that temperature and, furthermore, the time sensitivities of the various fuels are different. The determination of the maximum or minimum ignition temperatures, which correspond to zero or infinite time lags, respectively, is of theoretical interest, but the existence of neither of them has yet been proved.

B. Engine tests

The success of the gasoline knock-testing engine encouraged the search for a method that looks for an answer on Diesel fuel quality in the engine itself. The possibility of using the gasoline knock-testing engine unaltered suggested itself. From the reverse behavior of the fuel in spark-ignition

and compression-ignition engines it was not unreasonable to expect that Diesel fuels would rank in the reverse order as their octane numbers or directly as their "heptane numbers". One practical drawback to this method has been the difficulty of carbureting heavy oils and the trouble these oils cause in the engine by gumming, coking, crankcase dilution, etc. Dumanois (14) overcame these difficulties by mixing 15 per cent Diesel fuel with reference gasoline. The knock rating of such mixtures in the gasoline knock-testing engine was found to correlate fairly well with the behavior of the heavy oil in the Diesel engine. But at the same time the tests have shown (25) that it is too much to hope for a perfect reciprocity in a spark-ignition and compression-ignition engine that would justify the universal adoption of the gasoline-testing method for Diesel fuels. If a larger margin of error is admissible this simple method of rating Diesel fuels is recommended

There is no apparatus that simulates the compression-ignition engine conditions as much as a compression-ignition engine itself. The use of a compression-ignition engine for testing the ignition quality of fuels started in 1931 and attained considerable momentum recently. A variety of methods have been used by Le Mesurier and Stansfield (29), Boerlage and Broeze (6), Pope and Murdock (40), Joachim (27), Rendel (41), and Schweitzer and Hetzel (47). In principle, however, all of these agreed. The ignition quality as such is not measured by any engine test, but is only determined indirectly on the basis of the behavior of the fuel in the test engine in regard to such characteristics as combustion knock, ignition lag, rate of pressure rise, starting, or misfiring.

A valid objection to engine test methods is that the results they give have no *theoretical* significance, and can not be expressed in terms of ordinary physical units. However, in view of the great *practical* significance of fuel rating, this objection can be set aside as it was set aside in the case of knock rating of gasolines.

Another objection that has been raised against this type of testing is that its practical significance is limited to the type of engine with which the tests have been performed. Doubts regarding the general nature and applicability of the ratings obtained by engine tests have been largely dispersed by investigations performed on a great number of engines by Boerlage and Broeze (6), Stansfield (48), Joachim (27), MacGregor, and Good (31). The results have shown (46) that (1) with few exceptions, for which the reasons are clear, all engines rate fuels in substantially the same order, (2) the results obtained in any engine are not unduly sensitive to the engine factors such as amount of fuel, type of spray, injection timing, etc. These statements are rather general and do not apply equally to all types of engine tests that have been proposed, but accumulated evidence tends

to indicate that the behavior of Diesel engines with regard to cetane rating is much more uniform than the behavior of spark-ignition engines with regard to octane rating

1 Test engine

Broadly speaking, any engine is suitable for fuel testing. This fact was recognized by the Institute of Petroleum Technologists (25a) by permitting the use of any engine for the determination of fuel ignition quality. In this country the converted C F R engine, built by the Waukesha Motor
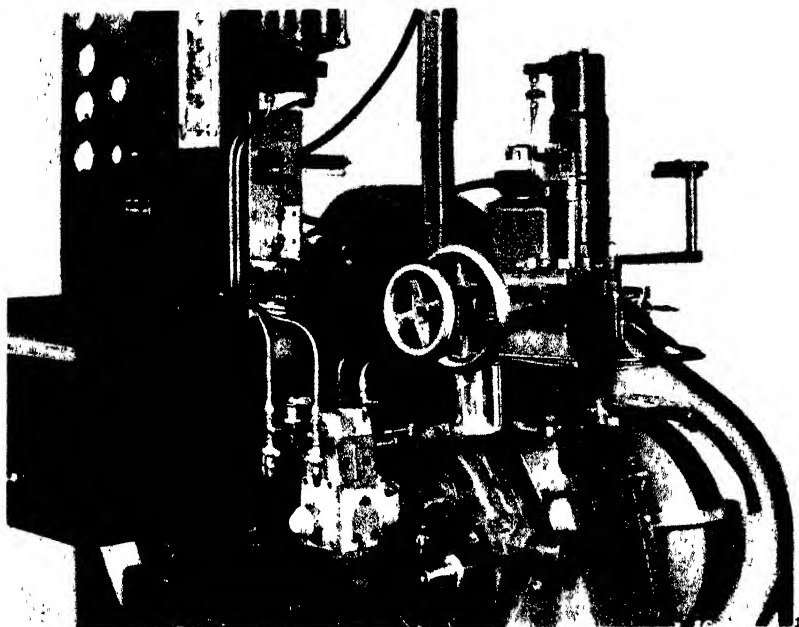
Fig 1 C F R engine for Diesel fuel testing developed by the Waukesha Motor Company

Company, has been used almost universally for fuel testing The engine is shown in figure 1 and the cross section of the head in figure 2. It is a $3\frac{1}{2}''$ x $4\frac{1}{4}''$, one-cylinder, four-cycle engine with a swirl type combustion chamber provided with an adjustment plug which permits changing the compression ratio between 6:1 and 28:1 An induction type generator supplies the load and maintains the speed constant Otherwise the engine is conventional except that it is provided with heaters for the intake air, cooling water, and lubricating oil which permit keeping these at a pre-determined value.

The chief advantage of the Waukesha type of test engine is its variable compression ratio. An engine with a fixed compression ratio can only test fuels of a limited range, while the variable compression ratio not only enables the engine to burn a wide range of fuels but by suitable adjustment the engine can be made sensitive to the ignition quality of the test fuel.

2. On the selection of a suitable ignition index

In testing the ignition quality of fuels in an engine the fuels are compared on the basis of some suitable index such as knock, pressure, ignition lag, etc. The engine as a testing instrument cannot be expected to measure the ignition quality of a fuel in physical units. But a rating can be based on engine tests if the engine is able to indicate that one fuel has a higher ignition quality than another. With the use of the cetane scale the engine
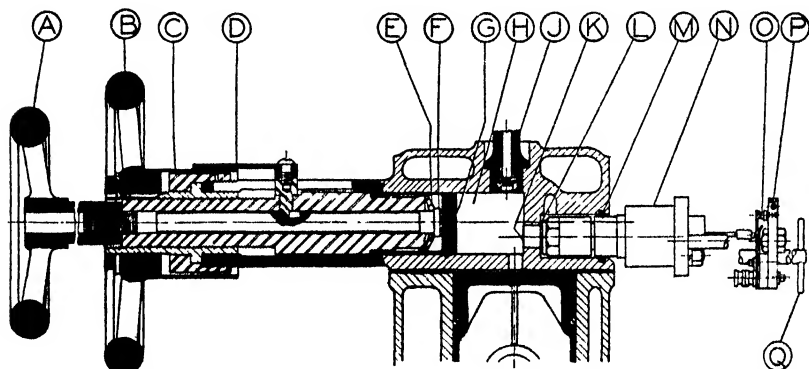
Fig. 2. Diesel variable compression plug. Optical delay method. Cross section of cylinder head showing mechanism for varying volume of combustion chamber.

test is boiled down to answering the simple question: Are the ignition qualities of two given fuels equal? If not, which is higher?

Several criteria can be used for answering this question. Those that have received wider attention are (1) combustion knock, (2) pressure rise, (3) rate of pressure rise, (4) ignition lag, (5) misfire, and (6) computed combustion knock. These will be discussed briefly:

(1) *Combustion knock* is a factor with which the user is directly concerned. It can be judged from a casual inspection of the running engine. The aural observation, however, is too inaccurate to serve as a basis for test. Le Mesurier and Stansfield (29) compared fourteen Diesel fuels on the basis of audibility of combustion knock estimated by ear. In the Junkers engine, which had an integral combustion chamber, the comparative rating of the fuels was the same at any speed between 300 and 1000

R.P.M. On the other hand, in the McLaren-Benz engine, which is of the precombustion chamber type, the order of merit changed with the speed.

Another difficulty with audibility tests is that it is not always easy to discriminate between combustion knock and other engine noises. To eliminate the latter difficulty and also the personal element in sound estimation, Carpenter and Stansfield (12) developed the strobophonometer, which measures the noise of a certain phase of the cycle by means of a mechanically driven selector and a suitable microphone. The noise readings obtained with this instrument correlated fairly well with ignition lag measurements and rate of pressure rise measurements.

(2) *Pressure rise* is frequently used as a measure of engine roughness. The maximum explosion pressure cannot be used as a measure of roughness (6), because an increase in intake air pressure increases the maximum pressure but at the same time makes the engine run more smoothly. It was also observed that the effect of fuel on the maximum pressure is indefinite. Good, bad, and indifferent fuels sometimes happen to have about the same combustion pressure rise. For these reasons pressure has never been considered as a suitable index of ignition quality.

(3) *Rate of pressure rise* is defined as the derivative of the pressure on the basis of time or crank angle. It is an indirect measure of the rapidity of burning. It was observed that combustion knock is always accompanied by a rapid rate of pressure rise. The correlation between shock audibility and maximum rate of pressure rise was found to be about 90 per cent (29, 45). The correlation between ignition lag and maximum rate of pressure rise was equally high.

In early investigations maximum rate of pressure rise was determined by drawing tangents to crank angle base indicator cards. The observation was made that if the M.R.P.R. (maximum rate of pressure rise) is less than 30 lb. per square inch per degree of crank motion, the operation is smooth. The engine is liable to knock if the M.R.P.R. is above 50 lb. per degree and is almost certain to knock if the rise exceeds 100 lb. per degree crank angle.

At present instruments are available which give the maximum rate of pressure rise directly, instead of deriving it from a pressure curve. By using an electromagnetic pick-up in connection with a diaphragm in the cylinder head, the flexing of the diaphragm which follows the pressure generates voltage in proportion to the flexing (flux-cutting) velocity. This voltage can be impressed on a cathode ray oscillograph and the M.R.P.R. scaled as the maximum deflection of the light point on the screen.

The Sunbury knock indicator (3), which has been introduced recently for knock rating gasolines, is using this principle. Here the magnified

output of the magnetic pick-up is fed into a damped millivoltmeter and the reading is a measure of the average rate of pressure rise. The use of this instrument for Diesel fuel testing deserves serious consideration.

(4) *Ignition lag* is the time interval between the point of injection and the point of ignition. It has been used as the preferred index of ignition quality since the investigations of Le Mesurier and Stansfield (29) and of Boerlage and Broeze (6) have established the close relations that exist between ignition lag and fuel quality as evidenced by combustion knock and difficulty of starting. The shorter the ignition lag of the fuel, the more quietly the engine runs and the more easily it starts if other conditions are the same. The principle of most current methods of measuring ignition quality is to match the sample fuel with a reference fuel which has the same ignition lag in a standard test engine under standard operating conditions or in the user's engine under the user's normal operating conditions.
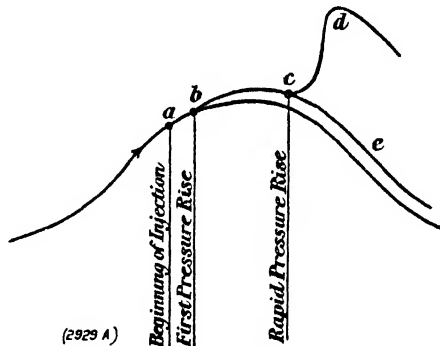
FIG. 3. Definition of point of ignition (Boerlage and Broeze)

The ease with which the ignition lag can be measured was no doubt a factor in its adoption for testing. In spring-loaded nozzles the beginning of the injection coincides with the beginning of the valve lift and can be determined very accurately by electrical means if the valve stem is accessible, as it usually is. The ignition point, on the other hand, was obtained from the indicator card, which regularly shows a readily noticeable pressure rise where ignition sets in.

While in most cases the determination of the ignition point from the indicator diagram offers no difficulty, in cases like that shown in figure 3 a more exact definition is needed. Ignition point is frequently defined as the point where the pressure rises above the compression pressure (point b, figure 3). Boerlage and Broeze (6) are of the opinion, however, that the ignition point so defined is not significant of the knock or of the ignition quality of the fuel. They advocate the use of the first *appreciable* pressure

rise (point c, figure 3) as ignition point. Hetzel (19) has, in fact, shown by oscillograms that by successively decreasing the compression ratio the point of appreciable pressure rise occurred later and later while the point of *initial* pressure rise was the same. Ignition point has also been variously defined as the time of first flame formation as detected by the human eye on a photographic film (22) or by a photocell (44), but for routine testing this is probably still less significant, as incandescence is of no immediate concern.

For the purpose on hand the definition of Boerlage and Broeze seems the most appropriate, although it is realized that in certain cases it must be arbitrarily decided when the rate becomes "appreciable."

(*5*) *Misfire* occurs if the compression ratio is not high enough to cause ignition. Since fuels of low ignition quality misfire at higher compression

Pressure Time Diagram
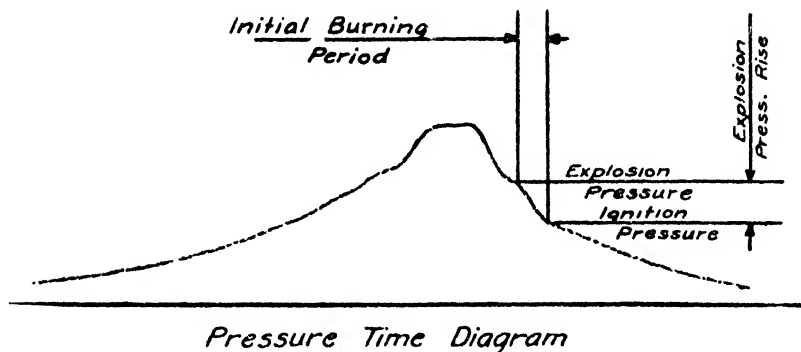
Fig. 4. Definition of compound combustion knock (Joachim)

$$c.k. = \frac{(\text{explosion pressure rise})^2}{\text{initial burning period} \times 10^4}$$

ratios than fuels of high ignition quality, misfire can and is being used as an index of ignition quality. In using the cetane scale the procedure again consists of matching the sample fuel with a reference fuel which misfires under identical conditions. A misfiring condition may be brought about by various methods. In a running engine one may reduce the compression ratio (if it is a variable compression engine), or decrease the intake air pressure (by throttling), or retard the injection timing, or decrease the jacket water temperature to the point at which misfiring occurs. The other alternative is motoring the engine with injection shut off until it reaches stable temperature. Then the ignition is turned on. If no ignition takes place the compression ratio (or the other factors) is raised until ignition does take place. The borderline of misfiring is thus determined.

Two methods involving misfiring have become popular for fuel testing.

The C.C.R. (critical compression ratio) method (40) is using a motored engine, and the test is sometimes referred to as the starting test, as it simulates starting conditions. The throttling method throttles the intake air of a running engine until the engine misfires. This method sometimes is referred to as the altitude test. Both of these misfiring tests give a high correlation with the ratings obtained by the delay methods.

(6) *Computed combustion knock* has been introduced by W. Joachim (27) and is defined as the product of the "explosion pressure rise" and the rate of pressure rise which takes place during the "initial burning period" (see figure 4). Its numerical value is obtained by the formula

$$\text{Computed knock} = \frac{(\text{explosion pressure rise})^2}{\text{initial burning period} \times 10^4}$$

where explosion pressure rise is expressed in pounds per square inch and initial burning period in degrees crank angle. The formula has merit, and remarkably good correlation has been shown (31) between it and ratings obtained with conventional methods. Its chief disadvantage is that the "initial burning period" is seldom sharply defined and is frequently difficult to determine (34).

3. Three requirements of a good testing method

Any satisfactory testing method has to satisfy three requirements: (1) convenience, (2) reproducibility, and (3) validity.

For convenience a testing method is preferred which is quick and simple, and does not require elaborate instrumentation and numerous delicate adjustments.

It is only a truism that a good testing method *should* give reproducible results. It is no less a truism that a properly standardized test cannot but give reproducible results. The essence of the matter, however, is that it is not desirable or even possible to standardize a great number of factors to an absolute accuracy, with no tolerance permitted. If slight variations in some factors cause a great variation in the test result, the reproducibility is poor. The same term is applied if the test result is affected by factors the control of which is difficult or impossible. The term "reproducibility" is used in this sense in this discussion.

"Validity" means that the results of the test are representative and give exactly the information the observer is seeking. If the observer is interested in the wear resistance of a metal, the Brinell hardness test is valid, but a test of tensile strength is not. It is not easy to determine the validity of a test on ignition quality, because we have no exact definition of what ignition quality is. It is generally understood that Diesel fuels of high ignition quality start more easily, run more smoothly, and begin

to misfire later than fuels of low ignition quality. But there is no conclusive evidence that these three things mean one and the same thing and, for that matter, we do not even know what any one of them means. The fact that has been established by numerous investigations is this: If by any arbitrary tests a group of fuels is ranged in the order of their resistance to misfire, then in the order of their ease of starting, then in the order of their smoothness of running, the three orders will be not exactly, but substantially, the same. It also has been shown that engines of various types and sizes rate the fuel in substantially the same order. These observations form the justification of the ignition quality testing. But not every test shows equally good correlation. The validity of a testing method will be considered high if its correlation is high with other tests and tests on other engines. The behavior of the fuels in service engines is considered most significant from the standpoint of validity.

To judge the various fuel-testing methods that have been proposed they are to be examined as to the extent to which they satisfy the three basic requirements of convenience, reproducibility, and validity. Some of these can be decided even without considering the details of the particular testing technique.

Tests based on the audible knock have not been used to any extent in routine testing because they are inconvenient. No simple measuring instrument is available for the purpose.

Tests using the maximum pressure or combustion pressure rise for index of ignition quality must be ruled out on the lack of validity.

Maximum rate of pressure rise, on the other hand, correlates fairly well with valid indices, and the test can be made conveniently with simple instruments. While this type of test has not yet been proposed formally we have given considerable attention to it. As a result, the author's opinion is that the weakness of the M.R.P.R. test is its poor reproducibility.

For perfect reproducibility the engine and operating conditions have to be standardized with any testing method. But a desirable ignition index is one that is most sensitive to fuel quality and least sensitive to engine factors, particularly to those that are difficult to control.

The more important engine factors are as follows: engine speed, jacket temperature, inlet air temperature and pressure, compression ratio, combustion chamber shape, injection timing, injected fuel quantity (load), and nozzle opening pressure. Of these, injection timing seems to give the most trouble.

On many engines the injection timing can be controlled and read, on some it can be controlled but not read, and on some others it can be neither controlled nor read. Test engines as a rule permit setting the injection point at will, but an error of up to 0.5° can be committed easily. When

changing from one fuel to another of different viscosity or gravity, the injection advance angle changes with unchanged injection setting. For these reasons an index of ignition quality which is not unduly sensitive to injection timing is clearly preferred.

4. Effect of injection timing

Injection timing in an engine is controlled ordinarily by the fuel injection pump, but the beginning of pump delivery should not be taken as the beginning of the injection. The actual injection, corresponding to the
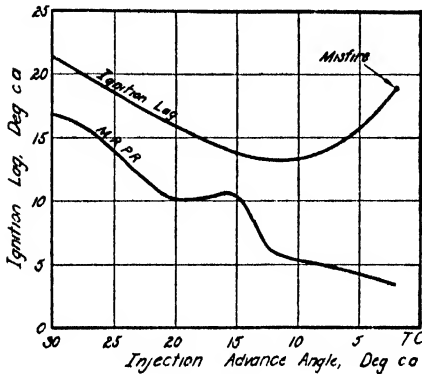
FIG. 5.
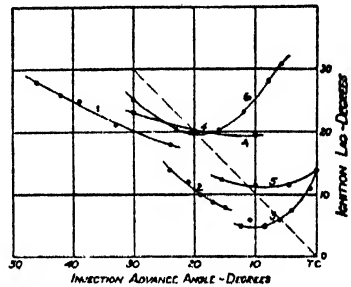
FIG. 6.

FIG. 5. Effect of injection timing on ignition lag and maximum rate of pressure rise (arbitrary scale)

FIG. 6. Effect of injection timing on ignition lag in various types of engines. Curve 1, open combustion chamber, slight air swirl (Dicksee); curve 2, divided combustion chamber, moderate air flow (Dicksee); curve 3, divided combustion chamber, vigorous air flow (Dicksee); curve 4, open combustion chamber, negligible air flow, Bosch pump (N.A.C.A.); curve 5, open combustion chamber, negligible air flow, N.A.C.A. pump (N.A.C.A.); curve 6, open combustion chamber, negligible air flow, earlier N.A.C.A. pump (N.A.C.A.).

exit of the first drop of fuel from the spray nozzle, always takes place later, the injection lag varying with the injection tube length, engine speed, fuel viscosity, injection quantity, etc. Therefore a fixed pump injection does not mean a constant injection timing. The injection point may vary 5 degrees crank angle or more according to engine speed, fuel viscosity, injection quantity, etc.

The effect of the injection advance angle on the maximum rate of pressure rise is erratic. Figure 5 is an example, where the waved line shows the maximum rate of pressure rise in an arbitrary scale and the heavy line the ignition lag in degrees crank angle. When the injection is advanced

from top center to 12 degrees before top center the M.R.P.R. rises, because
the combustion approaches constant volume conditions. But at the same
time the ignition delay period is also advanced, coming closer and closer
to the high temperature zone near top center and becoming shorter and
shorter. The shorter ignition lag reduces the amount of vaporized fuel
accumulated at the moment of ignition and tends to reduce the rate of
pressure rise. Indeed, if the injection is advanced beyond 17 degrees, the
latter effect predominates and the M.R.P.R. falls. · If the injection is
advanced still farther, the ignition delay period is ahead of the hot top
center zone, and consequently the M.R.P.R. increases again because of the
excessive ignition lag.
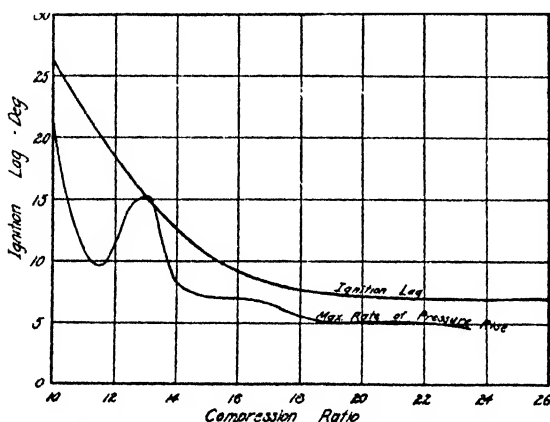
Fig. 7. Effect of compression ratio on ignition lag and maximum rate of pressure rise

The effect of the injection timing on the M.R.P.R. is complex. It will
be noted that the latter jumps suddenly between 12 and 14 degrees before
top center, which is the customary injection timing.

Figure 5 refers to a turbulent chamber engine. In non-turbulent
engines the variation of the M.R.P.R. with injection timing is still more
erratic (46) (figure ·11). If M.R.P.R. were used as an index of ignition
quality, the injection advance angle would have to be held within close
limits.

Of course ignition lag is also affected by the injection timing but to a
much lesser degree, as is seen in figure 5 and also in figure 6, which are
reproduced from another paper (46). With the normal injection advance
the ignition lag is close to its minimum and therefore insensitive to slight
variations in timing.

The maximum rate of pressure rise shows a similarly erratic behavior
with regard to compression ratio. In figure 7 the wavy line is the M.R.P.R.

at an arbitrary scale and the heavy line is the ignition lag in degrees crank angle, as they vary when the compression ratio is varied from 10:1 to 24:1, while ignition always takes place at top center. When the compression ratio is about 12:1, three different compression ratios correspond to a single M.R.P.R.

Experiments have shown that the validity of the M.R.P.R. index is also poor. N.A.C.A. tests (38) revealed cases where a change in air flow caused ignition lag and combustion knock to decrease and at the same time the rate of pressure rise to increase. It has also frequently been observed that an increase in intake air pressure or temperature increases the M.R.P.R., although at the same time ignition lag and combustion knock go down.

At extreme conditions the M.R.P.R. index fails to respond. We have measured the ignition lag and M.R.P.R. of the primary standard reference fuels at 24:1 compression ratio, 200°F. intake air temperature, and 9 in. of mercury supercharge. The results are tabulated in table 2. The table

TABLE 2

Measurement of ignition lag and M R.P.R of the primary standard reference fuels
24:1 compression ratio; 200°F intake air temperature; 9 in. of mercury supercharge

FUEL	CETANE NUMBER	IGNITION LAG		M.R.P R.	AUDIBLE KNOCK
		Degrees crank angle	Milli-seconds		
Cetane .	100	4.8	0.9	21	Very smooth
Alpha-methylnaphthalene .	0	8	1 48	25	Very rough
Straight-run Mid-Continent gas oil . .	55	5	0 93	20	Very smooth

shows that under conditions that are extremely favorable to combustion the difference between the best and the poorest fuel is still very pronounced to the ear and quite pronounced in ignition delay but fades away in the maximum rate of pressure rise.

Ignition lag is a convenient index of ignition quality when determined with the instrumentation to be described later. The reproducibility of the results is satisfactory if ordinary precaution is exercised. The recent report of the Volunteer Group for Compression-Ignition Fuel Research (2) showed an average deviation of 1.7 cetane numbers for twelve fuels and twenty-two laboratories using delay methods. This will, no doubt, be further reduced with improved instrumentation.

The validity of the results obtained with the ignition lag method cannot be decided conclusively as yet, but reports available (6, 48, 31, 37, 2) indicate that it is of a high order.

Misfiring is a most convenient ignition index inasmuch as it needs hardly

any instrumentation. It is simple to throttle the intake air on any engine until misfiring occurs. Of course the range of fuels that can be tested in this way is rather narrow, unless the compression ratio is varied. The objection to this type of test is that an engine running a great deal on the borderline of misfiring deposits so much soot that frequent cleaning is necessary. This is obviated by the C.C.R. method, which uses a motored engine and allows injection only during a few revolutions. The lowest compression ratio at which firing takes place is the ignition index.

There is, however, a certain conflict in the C.C.R. method between convenience and reproducibility. To obtain reproducible results, the heat and the residual gas condition of the engine must be strictly identical. A trial injection, however, upsets the equilibrium, whether it results in firing or not. Therefore an extremely rigorous routine must be maintained which involves considerable loss of time incurred during the waiting periods. These difficulties were greatly relieved by a special injection control device designed by MacGregor (30), which automatically by-passes thirty out of every thirty-two injections.

With regard to validity the record of the misfiring method is better than fair (48), but the motored engine seems to be somewhat behind the running engine as far as correlation with the delay rating is concerned. The recent Volunteer Group Report (2) showed that the C.C.R. ratings were generally 2 to 3 cetane numbers higher than the ratings by the delay method except for the doped fuels which were shown up poorly by the C.C.R. method. Since the cylinder walls are cooler and the ignition lag is nearly 180 degrees, the C.C.R. test may represent starting conditions rather than those of a running engine.

Not much can be said in favor of the "computed combustion knock" in regard to convenience. It involves a laborious evaluation of indicator cards. No data are available to estimate its reproducibility. Its validity is of a high order, according to recent reports (37), as it gives good correlation with ignition lag ratings for both doped and undoped fuels.

C. Physicochemical methods of fuel rating

More space has been given to engine ratings because they alone are considered authentic, but physicochemical methods of fuel rating are also of interest.

The most popular indices in use are (1) the Diesel index with the formula

$$\text{Diesel index} = \frac{\text{A. P. I. gravity} \times \text{aniline point}}{100}$$

(2) the viscosity-gravity index with the formula

$$G = 1.082A - 0.0887 + (0.776 - 0.72A) \log \log (KV - 4)$$

where A = viscosity-gravity index,
   G = specific gravity at 60°F., and
  KV = kinetic viscosity at 100°F. in millistokes,
and (*3*) the boiling point-gravity index with the formula

$$G = A + (68 - 0.703A) \log B.P.$$

where A = boiling point-gravity index,
   G = A.P.I. gravity at 60°F., and
  $B.P.$ = 50 per cent distillation point in °C.

The correlation of these chemical indices between themselves and with engine tests has been investigated by Hubner and Murphy (25), Schweitzer and Hetzel (47), Yamazaki and Ôta (52), and the U. S. Naval Experiment Station (37). Applied to petroleum products all three indices give fairly good correlation with engine tests, but they generally fail on doped fuels or oils of vegetable origin. Specifically the addition of a small per cent of ethyl nitrate increases the cetane number of a 50 cetane fuel about 8 cetane numbers per 1 per cent of ethyl nitrate added (37), but the change in all three chemical indices occurs in the wrong direction.

Nevertheless the physicochemical indices fill a useful place, as they permit estimation of the ignition quality of the present commercially available fuels from simple physical and chemical data that are either available or can be determined with little trouble. None of the present indices is, however, good enough to take the place of the engine testing when accuracy is essential. Another consideration is that fuels which are now in use may not be typical in the future. The use of dopes, hydrogenation, polymerization, oils of coal and vegetable origin, and other unforeseen developments may so change the Diesel fuel picture that no empirical rating can be relied upon.

V. DEVELOPMENT OF TESTING TECHNIQUE

The discussion in the foregoing section attempted to explain why the variety of methods available for testing the ignition quality of Diesel fuels has narrowed down to a few alternatives of the engine delay method. All of the methods that enjoy some recognition at present are based on the ignition lag index. The differences are minor and concern technique and instrumentation. A description of four of these methods—the indicator, the knockmeter delay, the Socony-Vacuum, and the Penn State method—is sufficient to cover the field.

(*1*) *The indicator method* is still the most popular in Europe. The ignition lag is determined from an indicator card on which by a special device the beginning of the injection is marked. The marking device is ordinarily actuated by the needle valve stem. If under identical engine setting the

sample fuel gives an ignition lag equal to that of a certain reference blend, the concentration of the high reference fuel is the rating. The reproducibility of the indicator method is about 3 cetane numbers. The chief disadvantage of the method is its inconvenience· it is too laborious for routine testing.

(2) *The knockmeter delay method* has been used predominantly by the Volunteer Group for Compression-Ignition Fuel Research, after the procedure had been worked out, principally by T. B. Rendel. It uses the converted C.F.R engine and an instrumentation shown schematically in figure 8. The apparatus includes a neon lamp which rotates with crankshaft speed, a contactor actuated by the opening of the nozzle to flash the neon lamp to indicate the time of injection, a protractor to show the
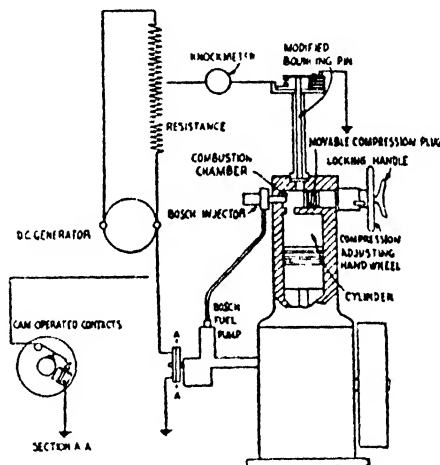
FIG. 8. Schematic circuit used with the knockmeter delay method

angular position of the flash, a modified bouncing pin which rests on a diaphragm in the cylinder head and which upon bouncing separates two contact points and interrupts the flow to the knockmeter, a knockmeter which is a heavily damped thermocouple type voltmeter, and a mechanical interrupter on the end of the fuel pump shaft to start the flow of current through the knockmeter. A direct current is passed through the interrupter, bouncing pin and knockmeter circuit and the dial indication is read. Two reference fuels, one giving slightly greater and one a slightly smaller knockmeter reading, are found by trial, and the unknown fuel is given a rating by interpolation.

The underlying principle is good. The knockmeter provides a convenient averaging if the injection or ignition points are erratic. In its

present form the method is highly standardized; the procedure is printed in Appendix I (see page 138).

The convenience and reproducibility of this method are adversely affected by the use of the bouncing pin. The friction between pin and barrel and the arcing between the contact points causes irregular action, unless a multiplicity of adjustments listed in the procedure is continuously attended to.

The use of the knockmeter is not as advantageous as it might at first seem. The integrating effect is of advantage if there is much spread in the ignition point of the successive cycles as with spark-ignition engines, but in a clean and properly operating Diesel engine the cycles repeat remarkably well and the spread in the ignition point is insignificant. However, the heavily damped knockmeter slows up the testing considerably (45). In changing fuels flushing of the line is discouraged because the absence of firing of only a few seconds puts the knockmeter hand off the scale, but with resumed firing equilibrium conditions are resumed very slowly.

In spite of these shortcomings the reproducibility of the knockmeter delay method is quite satisfactory. From the last report of the Volunteer Group (2) the average deviation of the knockmeter delay ratings was 1.8 cetane numbers. If, nevertheless, the same report recommends that "... the bouncing pin type of instrumentation should be definitely discarded in favor of the balanced diaphragm or the magnetic pick-up type," the recommendation is based more on the inconvenience than on poor reproducibility.

(3) *The Socony-Vacuum method*, devised by C. H. Schlesman, uses a balanced pressure diaphragm in place of the bouncing pin, but otherwise uses the same engine operating conditions as the bouncing pin delay method. The following description is from the report of the Volunteer Group (2).

"An insulated contact is placed on the tip of the injector feeler pin. A slight rise of the valve makes a contact which starts an electric current flow. A balanced pressure diaphragm is placed in the bouncing pin hole in the engine head. Pressure on top of the diaphragm is arbitrarily maintained at fifty pounds above compression pressure by connection to a CO_2 bottle. Combustion pressure causes contact to be made which stops the before-mentioned electric current flow. The successive delay times or current times are averaged by means of a special type condenser and a vacuum tube voltmeter. The start of injection is visibly indicated by a neon flasher and flywheel pointer which shows the injection time in degrees on a flywheel protractor for each cycle.

"Details of the apparatus may be obtained from the Socony-Vacuum Oil Corporation. Comments of those who have used the apparatus are very favorable in regard to ease of handling and the results compare well among themselves and also with averages by the bouncing pin delay method."

While the Socony-Vacuum method is no doubt superior to the knock-meter delay method in convenience, in reproducibility it is a little inferior, showing an average deviation of 2.1 cetane numbers from the "true" values.

(4) *The Penn State method* was devised by Hetzel and Schweitzer (20). In this method the bouncing pin was replaced by an electromagnetic pick-up, such as is used for phonographs and radio speakers of the magnetic type. A short stiff wire resting on the diaphragm transmits the motion of the diaphragm to the armature of the pick-up. The electromotive force generated in the coil surrounding the armature is used to control the operation of a thyratron tube. When the velocity of the diaphragm is high, as at the time of ignition, the thyratron relay trips and causes a neon lamp to flash. The timing of the flash is read on the protractor.
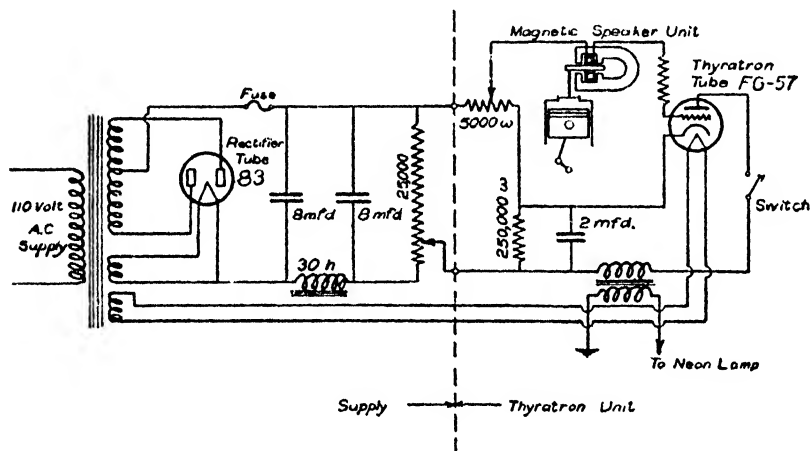
FIG. 9. Circuit of Hetzel and Schweitzer's magnetic pick-up ignition indicator

The circuit is shown in figure 9. The current generated in the coil reduces the negative voltage on the grid of the thyratron tube, thereby causing it to conduct, and permits a condenser to discharge. The current thus passing to the plate of the tube goes to a coil, which in turn sends a flash through the neon lamp. The neon lamp flashes once in every cycle, at the moment the velocity of the pick-up motion reaches a predetermined magnitude. At any other time the voltage generated is insufficient to trip the thyratron relay, and the neon lamp remains dark.

A pick-up identical with the one described is mounted on the end of the needle valve stem and indicates the injection. A small neon lamp of the low voltage type is connected to each pick-up and mounted on the fly-wheel, which is provided with a stationary angle scale for reading the position of the neon flashes to an accuracy of 1/10th of a degree.

The mechanism of the pick-up is practically frictionless. No electric contacts are used, and therefore troubles with arcing and pitting are eliminated. The wire and armature have a high natural frequency, so that they follow faithfully the motion impressed upon them. Both pick-ups are claimed to be insensitive to rough handling and to the manner in which they are mounted.

The technique followed in conjunction with the magnetic pick-ups is known as the "fixed ignition lag method." The injection timing is kept at, say, 18 degrees crank angle before top center. Ignition is always to occur at top center exactly. For low cetane fuel the required compression ratio to produce top center ignition (after 18 degrees ignition lag) is high; for high cetane fuels it is low. By moving the adjustable plug the compression ratio is adjusted until the neon lamp indicates ignition at top center.
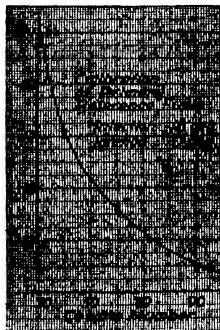
Fig. 10. Calibration curve of the required compression ratio versus cetane number

If the R.C.R. (required compression ratio) of the test fuel is equal to that of the reference blend, the ignition qualities of both are equal. Absolute matching may not be easy to obtain, but the unknown fuel can always be bracketed between two reference fuels and the rating approximated by interpolation.

If a number of samples are to be tested in one day, the use of a calibration curve is economical. By testing a number of the reference blends and noting the R.C.R. for each blend, a curve of R.C.R. versus cetane number is plotted on cross section paper. By determining the R.C.R. of the unknown fuel and marking it on the calibration curve, its cetane number can be read. Figure 10 is a typical calibration curve obtained under the operating conditions listed in Appendix II. For approximate rating a permanent calibration curve can be used. For accurate rating, however, a "day curve" or bracketing is necessary.

The advantages claimed for the Penn State method are the speed and accuracy with which the tests are performed and the simple reliable appa-

ratus which is used. All of the waiting associated with the other methods is eliminated, so that eight fuels can be rated in an hour, as compared with twelve per day rated by the indicator method (6) or one per hour rated by the knockmeter method (42). The Volunteer Group Report listed the reports of eight laboratories using the Penn State method and its modifications. The average deviation of these from the "true" ratings is calculated as 1.42 cetane numbers, which is less than that of any other method used.

VI. STANDARDIZATION OF OPERATING CONDITIONS

Although the ignition lag methods are not very sensitive to operating conditions, better reproducibility is attained if the operating conditions are standardized. A list of operating conditions recommended by Hetzel (19) is printed in Appendix II.
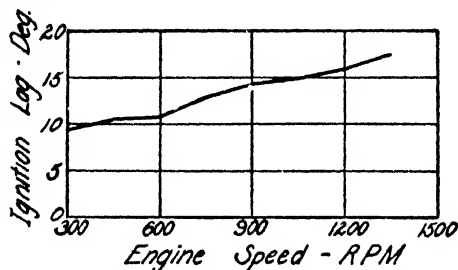
FIG. 11. Effect of engine speed on ignition lag

In selecting operating conditions under which the tests are to be conducted, the following three requirements should be satisfied as far as possible: (1) the conditions chosen should be typical of usual commercial engine practice, (2) they should be easy to maintain in the test engine, and (3) such values should be chosen that slight variations from the standard value will have a minimum effect on the results of the test.

Figure 11 shows that the effect of engine speed on ignition lag is small and its effect on rating probably negligible. A test speed of 900 R.P.M. is satisfactory.

Hetzel has found (19) that the effect of jacket water temperature on the ignition lag is quite pronounced, but the ratings obtained with 210°F. and 328°F. jacket water temperature seldom differed by more than 1 cetane number. A temperature of 210°F. is recommended, as it is easy to maintain with evaporative cooling.

Hetzel made a similar observation about the intake air temperature. Ratings obtained with 100°F., 150°F., and 200°F. air temperature seldom differed by more than 1 cetane number. Therefore the Volunteer Group standard of 150°F. is acceptable, although higher than is found in practice.

The effect of the lubricating oil temperature has never been investigated.

For ignition point, top center was found highly satisfactory, because it makes ignition pressure rise distinct and easy to identify. Incidentally, with ignition at top center ignition lag is about minimum (see figure 6), therefore a deviation in injection timing will cause minimum deviation in ignition lag. Hetzel investigated the effect of the ignition point ($-4°C$. to $+2°C$.) on both the ignition lag and rating and found the former to be small and the latter negligible.

For ignition lag Hetzel recommends 18 degrees, as against 11 degrees recommended by the Volunteer Group and 15 degrees recommended by W. G. Ainsley. In the selection the following considerations deserve attention.

The ratings themselves are practically independent of the ignition lag used in the tests performed with the fixed ignition lag method. Hetzel tested sixteen fuels with 10, 12, 14, 16, and 18 degrees ignition lag each. The maximum deviation from the mean was always less than 1 cetane number and the average deviation was only 0.36 cetane number. The disadvantage of the short ignition lag is that low cetane fuels require very high compression ratios for testing. The disadvantage of the 18 degrees ignition lag is that it is longer than the usual ignition lag in commercial engines. Hetzel's compression ratios were, however, unnecessarily high, because he used unnecessarily small injection quantities. More will be said about this later. With the proper injection quantities a standard ignition lag of 15 degrees seems very acceptable. In testing fuels of 30 cetane number or less, the ignition lag may be increased to 18 degrees and the results will still be comparable.

The nozzle valve opening pressure is tied up with the nozzle and the injection line. It may be anything between 1200 and 2500 lb. per square inch, provided the injection is regular. Double injections make testing difficult. Hetzel obtained regular injections with 1300 ± 100 lb. per square inch with a Bosch nozzle DM30S3 and a $\frac{1}{16}$ in. x 25 in. tube. For a given nozzle and tube the proper opening pressure can be determined by indicating the needle lift with a pick-up and oscillograph. In the range mentioned the ignition lag is independent of the opening pressure.

Fuel quantity injected per cycle has a greater effect on ignition lag than was suspected. Figure 12 shows the relation for a 55 cetane number fuel. Hetzel chose a fuel quantity as small as 20 mm.[3], "because this is sufficient to give regular injections, but is not so much as to produce violent combustion when poor fuels are burned." However, at low compression ratios the ignition lag is very sensitive to the injected fuel quantity, especially if the latter is small. This by itself is a disadvantage. The tentative standard of the Volunteer Group is 13 cc. per minute or 29 mm.[3] per injec-

tion.   Figure 12 shows that injection quantity should be increased at least to that amount which would bring it closer to the flat non-sensitive region. It also has the further advantage that it would reduce the required compression ratio and make the ignition lag standard of 15 degrees more attractive.   Of course an increased injection quantity requires more frequent cleaning of the engine.

The potentiometer settings should be such as to give earliest indications of injection and ignition, respectively   In exceptional cases it is possible to obtain "combustion flash" on compression alone, therefore as a precaution the ignition potentiometer setting should be checked so that with injection cut off no flash occurs.   With ignition at top center the combus-
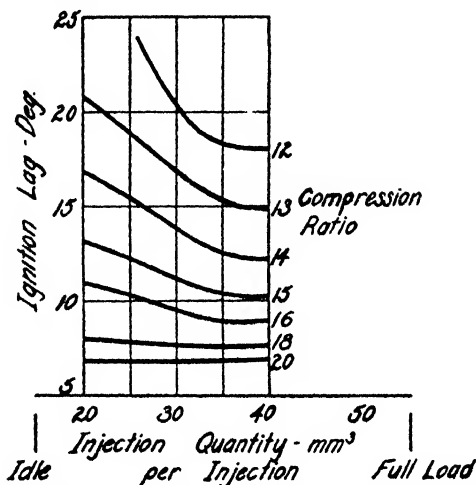
FIG. 12. Effect of injection quantity on ignition lag

tion pressure rise is so rapid that the ignition lag read is almost independent of the potentiometer setting and no precise adjustment is necessary.

VII. PRESENT STATUS OF DIESEL FUEL TESTING, TECHNICALLY AND COMMERCIALLY

In this country the working out of a method for testing Diesel fuels on ignition quality is in the hands of the Volunteer Group for Compression-Ignition Fuel Research, in which all major oil companies are represented. Under the chairmanship of T. B. Rendel this organization has worked hard for two years to solve the problem, and it is near to its goal now.   It is predicted that within a short time this group will be prepared to submit to the A.S.T.M. a tentative standard for adoption.

There is universal agreement that Diesel fuels be rated for ignition

quality in an engine on the basis of their ignition delay and that the rating be expressed in terms of cetane numbers. There is almost universal agreement that the high turbulent Diesel conversion of the C F R engine shall be used for testing. Although the non-turbulent type of engine has an advantage for fuel testing in being more sensitive to ignition quality, this is overweighed by the fact that the popular high-speed Diesel engines in this country are of the turbulent type.
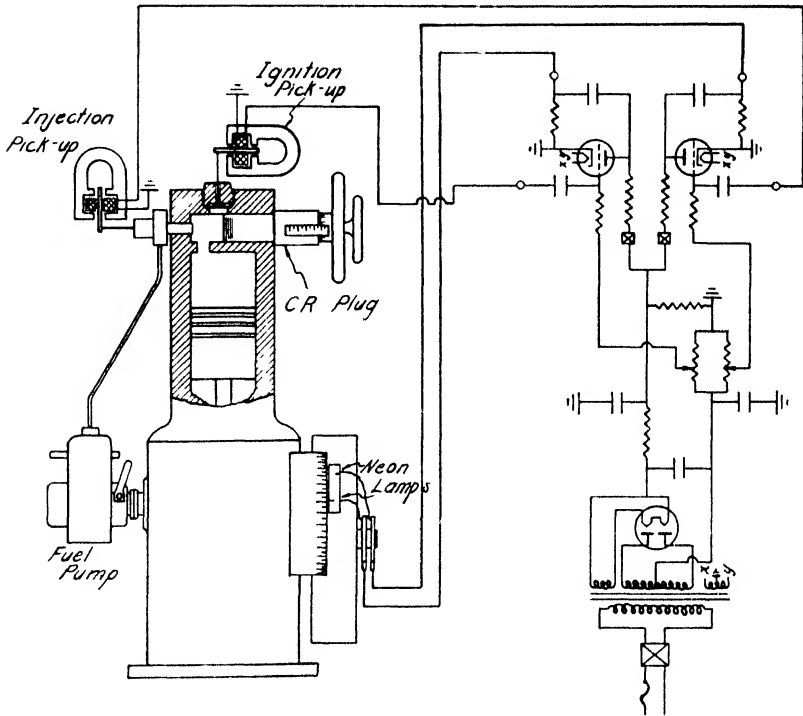
Fig 13 Schematic wiring diagram of the Aminco Penn State ignition lag indicator

The only item still left open is the exact type of instrumentation, but even therein considerable progress has been made lately. The bouncing pin has been definitely discarded in favor of the balanced diaphragm or magnetic pick-up type of instrumentation. The latter type has been simplified and made more convenient by the American Instrument Company. The American instrument employs the simplified wiring shown in figure 13, designed by R. L. Alcorn, Jr., and J. S. Chandler, and an improved protractor in which the injection neon lamp and ignition neon lamp are displaced by 15 degrees (an 18 degree offset can also be used). If the

compression ratio is properly adjusted for the fuel, the two neon flashes appear as a single luminous line

Figure 14 shows the pick-ups mounted on the C F R engine, while figure 15 shows the encased electronic relay, weighing 7 5 lb

In Europe the Diesel fuel testing is largely in the hands of the Institute of Petroleum Technologists The Institute agrees with the American Volunteer Group in the principle of engine method based on ignition delay,

FIG 14 Amnco Penn State ignition lag indicator mounted on a
C F R Diesel fuel-testing engine

but leaves open to the tester the choice of engine and the instrumentation According to the I P T plan the ratings are reported in ignition numbers, obtained by expressing the percentage of the high ignition quality reference fuel in the low ignition quality reference fuel, divided by ten and reporting to the nearest half number The I P T discourages the use of primary reference fuels (cetene), and favors the use of secondary reference fuels on account of the more consistent results obtained thereby on a variety of types of engines The Volunteer Group, however, does not

consider it practical to adopt secondary reference fuels over a long period of time and favors the use of primary reference fuels such as cetane and alpha-methylnaphthalene

It is notable that while Diesel fuel testing is more advanced in this country than abroad, in the use of Diesel fuels we are far behind. This refers to automotive application, especially to trucks and busses

In England, France, and Germany the majority of large trucks and busses produced in the last couple of years are equipped with Diesel engines, while in this country only a fraction of 1 per cent is so equipped. The chief incentive for the use of the Diesel engine abroad is its economy: the fuel
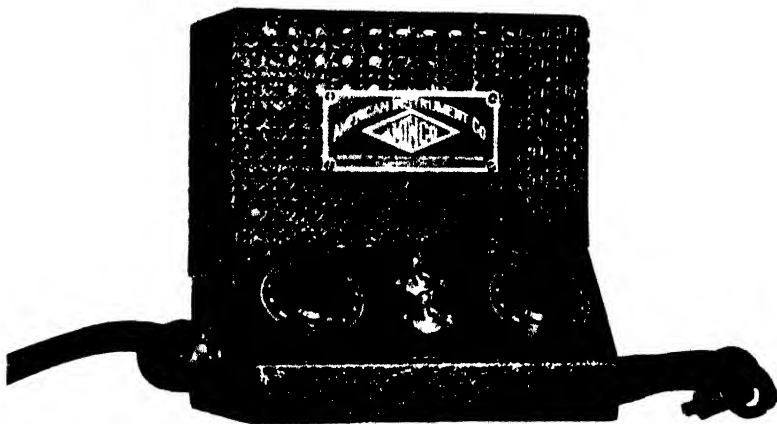
15

FIG. 15 Electronic relay of the Aminco Penn State ignition lag indicator

mileage is roughly double, and, furthermore, there is considerable difference in the price of Diesel fuel and gasoline. In this country gasoline is cheap and the introduction of the Diesel engine correspondingly slow. The one exception is the tractor field, where one prominent builder is turning out Diesel tractors at the rate of about a thousand a month

The present consumption of Diesel fuel in the U S is roughly estimated at 30 million barrels per year and is rapidly rising. Under these circumstances the commercial significance of Diesel fuel testing is expected to grow, even if it may not quite reach the commercial significance of the octane rating. The possible introduction of successful Diesel fuel dopes will greatly increase the demands on ignition quality rating.

REFFRENCES

(1) American Society for Testing Materials Minutes of the Meeting of the Co-ordinating Subcommittee on Diesel Fuel (a subcommittee of Technical Committee C of D-2) at White Sulphur Springs, June 19, 1935

(2) BAXTER, C H , AND RENDEL, T B Report of the Volunteer Group for Compression-Ignition Fuel Research, paper presented at the Meeting of the Society of Automotive Engineers, May 4 9, 1937

(3) BEALL, L S L , AND STANSFIELD, R The Sunbury Knock Indicator; paper presented at the Meeting of the Society of Automotive Engineers, May, 1937

(4) BECKER AND FISCHER S A L Journal **35**, 376 (1931)

(5) BECKER, A E , AND STACEY, H R Measurement of Ignition Qualities of Diesel Fuels, Paper No 211, World Petroleum Congress, London, 1933

(6) BOERLAGE, G D , AND BROEZE, J J Engineering **132**, 603 6, 687-9, 755 6 (1931)

(7) BOERLAGE, G D , AND BROEZE, J J S A E Journal **31**, 283 (1932)

(8) BOERLAGE, G D , AND BROEZE, J J Knock Rating for High-speed Compression Ignition Engine Fuels, Paper No 111 World Petroleum Congress London, 1933

(9) BOERLAGE, G D , AND BROEZE, J J Chem Rev **22**, 61 (1938)

(10) BRIDGEMAN, O C , AND MARVIN, C F , JR Ind Eng Chem **20**, 1219 (1928)

(11) BUTLER, W H Fuels for Automotive Diesels, paper presented at the Meeting of the Society of Automotive Engineers, June, 1931

(12) CARPENTER R F H , AND STANSFIELD, R Combustion in Heavy Oil Engines, paper presented at the Meeting of the North East Coast Institute of Engineers and Shipbuilders, February 26, 1932

(13) CONSTAM AND SCHLAEPFER Z Ver deut Ing **57**, 1489 (1913)

(14) DUMANOIS, P Compt rend **196** (April 3, 1933)

(15) FOORD F A J Inst Petroleum Tech **18**, 533 (1932)

(16) HAWKES, C J Engineering **110**, 749 (1920)

(17) HEINZE R Braunkohle **34**, No 38, 639 (1935)

(18) HESSELMAN Z Ver deut Ing **67**, 650 (1923)

(19) HEIZEL T B The Development of Diesel Fuel Testing, Penn State Coll E E S Bull No 45 (1936)

(20) HEIZEL, T B , AND SCHWEITZER, P H Automotive Ind **73**, 202 (1935)

(21) HILL, J B , AND COATS, H B Ind Eng Chem **20**, 641 (1928)

(22) HOLFELDER Forschungsheft No 374, Beilage zu Forsch Gebiete Ingenieurw **6**, Sept Oct 1935, translation in Natl Advisory Com Aeronaut Tech Mem 790

(23) HOLM, H Z angew Chem **26**, 273 (1913)

(24) HUBNER, W H S A E Journal **40**, 40 (1937)

(25) HUBNER, W H AND MURPHY, G B Natl Petroleum News **28**, No 4, 22, 24-6, 28, No 5, 25 8 (1935)

(25a) Institute of Petroleum Technologists Ignition Quality of Diesel Fuels, issued November, 1936

(26) JACKSON, E A Oil Gas J **33**, No 44, 16 (1935)

(27) JOACHIM Diesel Power **13**, No 5, May, 1935

(28) KREULEN, D J W J Inst Petroleum Tech **23**, No 162, 253 (1937)

(29) LEMESURIER L J , AND STANSFIELD, R J Inst. Petroleum Tech **17**, 387 (1931)

(30) MacGregor, J R.: Discussion presented at the Summer Meeting of the Society of Automotive Engineers, June, 1934.

(31) Good, R. F.: S. A. E. Journal 40, No. 6, 232 (1937).

(32) Marder, M., and Schneider, P.: Automobiltech. Z. 40 (April 25, 1937).

(33) Michailovra: Compt. rend. acad. sci. U. R. S. S. [N.S.] 2, No. 4, 96 (1936); translation in Natl. Advisory Com. Aeronaut. Tech. Mem. 813.

(34) Moore, C. C , Jr.: S. A E. Journal 40, 251 (June, 1937) (discussion).

(35) Moore, C. C., Jr , and Kaye, G. R : Oil Gas J. 33, No. 26, 108 (1934).

(36) Moore, H.: J. Inst. Petroleum Tech. 6, 186 (1919-20).

(37) Navy Department, Bureau of Engineering: Report E on Diesel Fuel Investigation, 1937 (available in mimeographed form).

(38) Natl. Advisory Com. Aeronaut Tech. Note 418.

(39) Neumann: Z. Ver. deut. Ing 70, 1076 (1926).

(40) Pope, A. W , Jr., and Murdock, J. A : S A. E Journal 30, 136 (1932).

(41) Rendel, T. B.: Proceedings of the Eighth Oil Power Conference; Penn. State Coll. Tech. Bull. No. 20, p 93 (1934).

(42) Rendel, T. B.: S. A. E. Journal 38, No. 6, 225 (1936); Report of Volunteer Group for Compression-Ignition Fuel Research.

(43) Rieppel: Z. Ver. deut. Ing. 51, 613 (1907).

(44) Rose, R. A , Wilson, G C , and Benedict, R. R.: S A. E. Journal 39, 459 (November, 1936).

(45) Schweitzer, P H : Proceedings of the Sixth Oil Power Conference; Penn. State Coll Tech. Bull No. 16, p. 73 (1932).

(46) Schweitzer, P H., Dickinson, H. A., and Reed, M. J.: Status of Diesel Fuel Oil Standardization in the United States; Paper No. 78, World Petroleum Congress, London, 1933

(47) Schweitzer, P. H , and Hetzel, T B.: S. A. E. Journal 38, No. 5, 206 (1936).

(48) Stansfield, R.: The Ignition Quality of Fuels, etc.; Paper No. 77, World Petroleum Congress, London, 1933.

(49) Sugden, S : J Chem Soc. 125, 1177 (1924).

(50) Tausz and Schulte: Z Ver. deut Ing. 78, 577 (1934).

(51) Wollers and Ehmcke: Krupp Monatsh. 2, 1 (1921).

(52) Yamazaki, K., and Ôta, S.: J. Fuel Soc. Japan 14, 134 (1935).

APPENDIX I

Tentative Standard Operating Conditions and Procedure for Delay Period
Method of Rating Diesel Fuels

I. OPERATING CONDITIONS

1. Engine speed . .	900 ± 3 R.P.M.
2. Cylinder	High turbulence variable compression Diesel cylinder
3. Jacket temperature	Constant within ±1°F.; limits 205–212°F.
4. Cooling liquid	Distilled water
5. Inlet air temperature . ' .	150 ± 2°F.
6. Crankcase lubricating oil .	S. A. E. 30
7. Oil pressure	25-30 lb. per square inch
8. Valve clearance	⎰Intake 0.008 in. cold ⎱Exhaust 0.010 in. cold

9. Injection advance	10°BTDC (constant)
10. Injection pressure .	1500 ± 50 lb per square inch (opening pressure)
11 Fuel quantity	13.0 ± 0.5 cc per minute
12. Injector cooling—water temperature	100 ± 5°F.
13. Injector specifications	Bosch DN30S3
14. Injection pump specifications	Bosch PE1B50A302/3S97, port closing at 0 075'' ± 0.005'' lift from base circle
15. Fuel line—tank to pump	3/8'' copper tubing
16. Fuel line—pump to injector	1/4'' O.D ; 1/8'' I.D.; length 36 in
17. Fuel tank height	25'' ± 1'' from bottom of tank to pump inlet
18. Knockmeter generator voltage	120 ± 1 volts

II. PROCEDURE

A. Starting and stopping the engine

While the engine is being turned over by the electric motor, the fuel by-pass valve on the injector is closed, and the compression ratio is increased until the engine begins to fire

To stop the engine, the fuel by-pass valve on the injector is opened and the electric motor then switched off.

B. Checking injection pump for port closing

The pump plunger port should close when the plunger has traveled up 0.075'' ± 0.005'' from the base circle of the cam. This setting is important, as it influences the injection rate. To check the port closing see paragraph #14 under "Installation Instructions" This adjustment is made in the factory and should not require resetting unless it has been tampered with.

C. Injection pressure setting

Remove injection pump cover and with injection line pressure gauge connected and injector arranged to spray into the air operate the pump plunger with a screw driver used as a lever. With the pressure gauge set at 1500 lb per square inch adjust the pressure on the injector spring until equal quantities of fuel spray from the gauge and injector. The opening pressure of the injector will then be the same as indicated on the gauge.

D. Injector indicator setting

1 Loosen the contact spring carrier clamp nuts and adjust until the spring leaf just touches the injector pin Then set the clamp nuts to provide ½ turn initial tension on the spring

2. Adjust the gap between the contact points to 0 004''.

E Bouncing pin preliminary static setting

Make static bouncing pin setting as follows:

1 Set gap between pin and arm 0.005'' with gap adjusting screw.

2. Bear down lightly on the end of the contact arm spring so that the arm is held on its seat. Adjust the spring tension screw until the screw just touches the spring. Then increase the tension by turning the screw down five notches.

F. Final compression ratio and bouncing pin adjustment

After the engine has reached equilibrium the compression ratio and bouncing pin setting at which an unknown fuel is rated are determined as follows:

1. Adjust the compression ratio about two compression ratios above that at which definite misfiring occurs.

2. With the engine firing, close the bouncing pin gap between pin and arm by turning the adjustment screw up until two distinct lines appear ahead of the "bump" on the optical indicator diagram. (This indicates that the bouncing pin arm is deflected by the compression pressure before combustion.)

3. With the engine firing, increase the bouncing pin gap between pin and arm by turning the adjustment screw down until the double line on the optical indicator just coincides with the base line. (This indicates that the bouncing pin arm is not moved by compression pressure, but is deflected the moment compression pressure is exceeded by combustion.)

4. Observe the angle at which combustion starts. The correct angle of combustion for making a rating is 1° after top dead center. Readjust compression ratio until this condition is obtained.

5. After a change in compression ratio, readjust the bouncing pin as outlined in paragraphs 2 and 3 above.

6. If the indicated angle of injection after the final bouncing pin setting has shifted more than $\frac{1}{4}$°, readjust the compression ratio and pin as outlined above.

7. Check the regularity of the bouncing pin on the neon tube indicator. If the angle of combustion fluctuates more than ±1°, adjust the bouncing pin tension screw by trial until steady readings are obtained.

G. Adjustment of contact breaker

The make and break points in the knockmeter circuit should be adjusted for an 8° contact period, as determined on the neon tube indicator. This can also be indicated on the knockmeter and should produce a reading of 80 to 100 on the scale when the generator voltage is 120 and the engine is not firing. The breaker timing should be adjusted to make contact approximately 2° before top dead center as indicated on the neon tube indicator. Check this setting on the knockmeter with 120 generator voltage. A knockmeter reading of 50 should be obtained with the engine firing when combustion occurs at 1° after top dead center. Advance or retard the breaker until such a knockmeter reading is obtained.

H. Cetane number determination

The cetane number of a fuel is ascertained by comparing the delay (as measured with the knockmeter) for the fuel with those for various blends of the reference fuels until two blends differing in delay by not more than the equivalent of 8 cetane numbers are found, one of which has a longer delay and the other a shorter delay period than the sample. The reference fuel which would exactly match the sample is computed by interpolation from the knockmeter scale readings of the fuels.

An alternate series of knockmeter readings is taken on the test fuel and reference fuel blends After changing from one fuel to the other, 5 minutes must be allowed to insure the complete change over, since there is a comparatively large volume of fuel in the pump and line.

At least three alternate series of readings should be taken on each fuel, and if the average knockmeter reading of the fuel sample is higher than that of the reference fuel blend, the test should be repeated with a blend containing decreased proportion

of the high cetane number of reference fuel. The test is continued in this manner until the knockmeter reading for the sample is definitely higher than for one blend and lower than for another blend of the reference fuels.

1 Precision of results

The cetane number should be reported in the nearest whole number to the exact rating as computed by interpolation from the knockmeter readings.

J. Miscellaneous notes and suggestions

1. *Clean* fuel must be used It is suggested that the fuel be filtered through thin chamois leather into the fuel tanks

2 The fuel lines and fuel pump must be thoroughly flushed of air before starting the engine. After the engine is running better results are obtained by switching quickly from one fuel to another *without flushing the fuel pump*, and allowing 5 minutes for the change over.

3. When changing fuels in the tanks, it is very necessary to flush thoroughly the line to the switch valve until a solid fuel stream is obtained from the bleed drain

4. The fuel injection timing should be shown continually on the spark quadrant and any deviation from 10° before top dead center must be corrected before each knockmeter reading is taken.

APPENDIX II

RECOMMENDED PROCEDURE FOR DIESEL FUEL TESTING BY THE FIXED IGNITION LAG METHOD

I. OPERATING CONDITIONS

1. Engine speed	900 ± 30 R.P M
2. Jacket temperature	Boiling point of water constant within ± 1°F.
3. Inlet air temperature	150 ± 0.5°F.
4. Lubrication oil temperature	150 ± 10°F.
5. Injection advance	18 deg. B T.C
6. Ignition	At top center exactly
7. Nozzle opening pressure*	1300 ± 100 lb. per square inch
8. Fuel quantity	0.020 cc per injection ± 10 per cent
9. Potentiometer	To give earliest indication of injection and ignition, respectively

II. PROCEDURE

1. The engine is motored for approximately 5 minutes while the air and water heaters and the thyratron tube warm up

2 The by-pass valve in the nozzle is then closed, the injection timing adjusted, and the compression ratio set to give reasonably smooth running while the engine warms up. The engine should run under power for at least 20 minutes in order to attain equilibrium temperature conditions of the engine and of the crankcase oil.

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* For Bosch nozzle DN30S3 and a 1/16 in. x 25 in tube. If a different nozzle or tube is used the injection pressure should be so chosen as to give uniform injections with a sharp beginning and a single principal opening.

3. Injection timing is adjusted by the pump timer until the neon lamp flashes at 18 degrees before top center. The ignition indicator is then switched on, and the compression ratio is varied until the neon flash indicates ignition at top center. The scale reading of the compression ratio adjusting plug is then recorded. Following that, the compression ratio is increased until ignition takes place several degrees before top center, and again decreased until ignition is indicated at top center and the scale reading of the compression ratio adjusting plug is again recorded. This is repeated so that altogether two determinations are made with increasing and two with decreasing compression ratios. The average of the four readings is then used to determine the required compression ratio for that fuel. The R.C.R is calculated by the formula R C.R. = 1 + 18/H, where H is the average of the four micrometer readings of the adjustable plug.

4. When switching from one fuel to another, the pump suction space is flushed for approximately 5 seconds, then, while the injection tube and nozzle are being purged of the fuel previously used, the other tank is drained, flushed, and filled with the next fuel to be tested.

5 After testing a series of blends of the two reference fuels, the volumetric percentage of the high cetane fuel in the low cetane fuel is plotted against the corresponding R.C.R values The R.C.R. of the sample fuel is placed on the curve which determines the rating of the sample fuel. If the sample fuels are tested first, the R.C.R. of some of the reference blends which are outside of the range of the sample fuels need not be determined If the approximate ratings of the fuels are known in advance, the preferred procedure is to test the fuels, including the reference fuels, in the order of their ignition quality. This combines the good features of bracketing, with curvilinear interpolation, and also directly compares fuels of similar or identical ignition quality so that relative merit may be more surely ascertained

DISCUSSION

T. B. RENDEL (Shell Petroleum Corporation, Wood River, Illinois): Three years ago a small group, known as the Volunteer Group for Compression-Ignition Fuel Research, was formed to study and eventually to standardize a method for rating the ignition quality of Diesel fuels. This group has pursued its work actively and has submitted three reports. The most recent of these reports was presented to the Society of Automotive Engineers and the American Society for Testing Materials, giving the results of the past eighteen months' work. In this report it is concluded that results of the past eighteen months' work indicate fairly definitely that a direct matching method on the basis of ignition delay is the best from the point of view of reproducibility and validity, and that therefore some sacrifice in simplicity and speed of testing must be made. In this connection it is to be remembered that the octane number test, after several years of development and with a far greater commercial incentive behind it, sometimes requires about 45 minutes for determination and is still liable to errors of 1 or 2 octane numbers.

Progress in methods of instrumentation has advanced considerably. It is recommended that the bouncing pin type of instrumentation should

be definitely discarded in favor of the balanced diaphragm or the magnetic pick-up type. Further work in a larger number of laboratories is desirable before definitely standardizing on this point. The cetane number is, however, not apparently affected outside the limit of error of the determination.

It is therefore recommended that Diesel fuel be rated for ignition quality on the basis of its cetane number, as determined by an ignition delay method on the high turbulent Diesel conversion of the C.F R. engine, the exact type of instrumentation for recording the delay to be left to the option of the user pending further work of the Volunteer Group.

The Volunteer Group has investigated Professor Schweitzer's mechanical pick-up type of instrument and is favorably impressed with its operation; cooperative work is now in hand with this instrument. Work is also planned on the correlation with actual service engines. In this connection, it is very encouraging to note that cetane rating is apparently insensitive to the type of engine and operating conditions, which in turn indicates that correlation with service engines is not far off.

THE KNOCK RATING OF MOTOR FUELS

H. W. BEST

Department of Mechanical Engineering, Yale University, New Haven, Connecticut

The knock rating of a fuel is essentially a direct comparison of the intensity of the knock produced by it with that of a standard fuel, these intensities being measured according to a specified procedure. Other methods, such as chemical analysis or bomb explosions, have been found to be inadequate for predicting the knock characteristics of a fuel when in actual service.

The fuels used as a standard of comparison are normal heptane and isooctane (2,2,4-trimethylpentane), first proposed by Graham Edgar (6). These fuels are pure hydrocarbons and thus can always be duplicated; they are similar to each other and to gasolines in their physical and chemical properties, and when blended can duplicate the range of antiknock qualities of gasolines likely to be used for motor cars, since isoöctane is considerably better and normal heptane poorer in this respect than ordinary motor fuels. Thus blends of these substances establish a standard scale for comparison of any motor gasoline.

In order that the results of different laboratories may correlate, not only is a standard reference fuel necessary, but the engine and the operating procedure must be standardized, because operating conditions affect the relative knock intensities of fuels. Therefore the Coöperative Fuel Research, single-cylinder, variable compression, vapor-cooled engine was designed specifically for this purpose. In order to obtain the knock rating of a fuel this engine is operated at 900 R.P.M. with a mixture temperature of 300°F. and the knock intensity of the fuel measured (1). The blend of normal heptane and isoöctane which matches the fuel in knock intensity under the same operating conditions is then determined, and the fuel is said to have an octane number which is the percentage of isoöctane in the isoöctane–heptane mixture which it matched.

A specified knock intensity is used which is obtained by varying the compression ratio and is measured by means of a bouncing pin. Secondary reference fuels which have been suitably calibrated against normal heptane and isoöctane blends are generally used instead of the expensive primary reference fuels. This method was developed by the Coöperative

Fuel Research Committee, on which are represented the Automotive Industry, the Petroleum Industry, and the National Bureau of Standards, and is the result of a great deal of coöperative work done by individual laboratories throughout the world.

In 1932 the Committee had developed the octane number scale, the knock-testing engine, and a procedure. The procedure at that time differed from the present procedure in that the engine was operated at 600 R.P.M. instead of 900 R.P.M. and the mixture temperature was approximately room temperature instead of 300°F. Also the spark timing was retarded 3.5 degrees with respect to that now in use. This method, now called the C. F. R. research method, was modified because results obtained with it did not correlate with results obtained in service.

ROAD RATINGS

In order to determine what effect actual service conditions have on the knocking characteristics of representative fuels, the C. F. R. Committee conducted in 1932 and again in 1934 comprehensive cooperative road tests at Uniontown, Pennsylvania (11, 10). A method of rating fuels on the road was developed which consists essentially in comparing the maximum knock intensity obtained with the fuel under test to the maximum knock intensity of reference fuel blends, irrespective of the speeds at which they occur. This method differs from that used in the laboratory in that the comparison of knock intensity is not made at any predetermined speed and the intensity is measured by ear rather than by instrument.

These road tests definitely established the fact that the variations in design of different makes of engine or even differences in adjustments in cars of the same make and model were sufficient to cause considerable differences in the relative knock intensities of fuels of different types. It was found that a cracked fuel, when run in one car, might knock with an intensity which was equal to that obtained with a reference fuel blend differing by 8 octane numbers from the blend it equalled when run in another car. Such differences were found even in two cars of the same make and model, showing that major variations in design were not necessarily the cause of these differences.

The knock intensity of any fuel varies with engine speed, but this characteristic is not the same for different fuels in the same engine or for the same fuel when used in different engines. With one fuel it may decrease continuously with increasing speeds, with another it may reach a maximum value at relatively high speeds or it may reach a maximum at two speeds.

Campbell, Lovell, and Boyd have obtained data which clearly illustrate these differences in knocking characteristics and which are reproduced in figures 1 and 2 (5). They ran a 100 per cent cracked fuel and blends of

straight-run reference fuels in a 1934 production car, having an ell-head engine with standard spark timing. These data are represented in figure 1, which shows that the reference fuels knocked throughout the speed range, the maximum intensity occurring at about 25 miles per hour and again at 50 miles per hour. The cracked fuel produced the maximum knock intensity at 50 miles per hour, but none at all below 35 miles per hour. The maximum knock equalled that of a 66 octane number reference fuel.
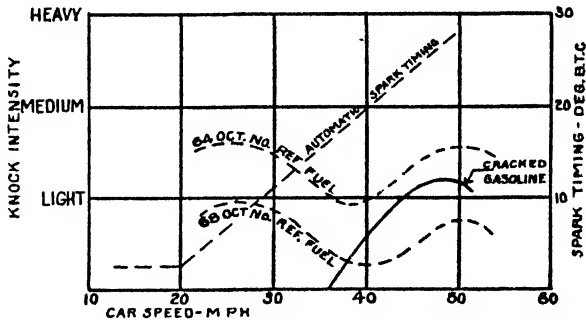
FIG. 1. Knocking characteristics of two types of fuels in a 1934 car (Campbell Lovell, and Boyd (5)).
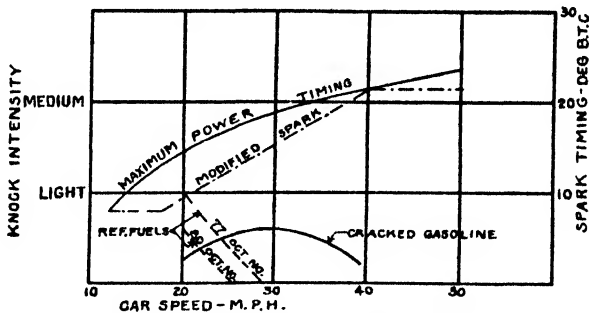
FIG. 2. Knocking characteristics of car represented in figure 1 with modified automatic spark timing (Campbell, Lovell, and Boyd (5)).

The automatic spark advance was then modified by advancing it 6° at low speeds and retarding it at high speeds with the results shown in figure 2. With this change, maximum knock with the cracked fuel occurred at between 25 and 30 miles per hour instead of at 50 miles per hour, and the intensity was decreased slightly. The reference fuels gave a continuous and rapid decrease of knock intensity with increasing speeds, but a 77 octane number blend now knocked with an intensity which equalled that previously obtained with a 68 octane number blend. The cracked fuel equalled in intensity of knock approximately an 80 octane number blend,

whereas with the standard spark adjustment it equalled a 66 octane number reference fuel blend. Thus this modification in spark timing in this particular engine caused the fuels to knock at lower speeds; it had but little effect on the knock intensity of the cracked fuel and considerably increased the knock intensity of the straight-run reference fuels, thus increasing the road knock rating of the former from 66 to 80 octane number. Therefore, the road rating of this fuel was changed by approximately 14 octane units because of the comparatively large effect on the reference fuels.

This example clearly illustrates the effect a change in adjustment of an engine may have on fuels of different types. In table 1 are tabulated some of the data obtained at Uniontown showing the effect of different representative engines (11). Column 3 gives the octane number of the straight-run reference fuels which were required for knock-free operation above 15

TABLE 1

Data obtained with different engines

CAR NO.	TYPE OF ENGINE	OCTANE RE-QUIREMENT (REFERENCE FUELS)	KNOCK INTENSITY		ROAD RATING	
			Experimental cracked fuel	Commercial fuel	Experimental cracked fuel	Commercial fuel
1	Overhead valve	76 78	Trace	Trace	75	76
2	Ell-head	76-78	Trace	Trace	77	76
3	Ell-head	76-78	Heavy	Trace	64	76
4	Ell-head	76-78	Heavy		64	
5	Ell-head	66-68	Heavy		55	

miles per hour. Column 4 gives the knock intensity obtained with a 100 per cent experimental cracked fuel when used in the same cars. Column 5 gives the knock intensity obtained with a commercial fuel, and columns 6 and 7 give the road ratings of these fuels in each car in terms of octane number of the reference fuel blends which they matched.

A study of this table shows that the reference fuels knocked with the same intensity in cars 1, 2, 3, and 4, but the cracked fuel knocked considerably more in cars 3 and 4 than in 1 and 2. Therefore its rating was reduced from about 76 to 64, when run in the two latter cars. When run in car 5 this same cracked fuel knocked with approximately the same intensity as it did in cars 3 and 4. However, the reference fuels knocked considerably less in car 5. Thus the rating was still further reduced to 55, because in this case the reference fuel was affected but not the cracked fuel.

The data in column 3 indicate that cars 1, 2, 3, and 4 require a better

fuel than does car 5 if the fuel is of the same type as the reference fuel. However, if the cracked fuel is used, car 5 requires a better fuel than do cars 1 and 2.

The examples cited above are extreme cases illustrating how different conditions affect the relative knock characteristics of fuels of different types. Such large differences are not common. The maximum differences observed during the Uniontown tests with typical commercial fuels were the equivalent of 5 to 8 octane numbers.

Since two fuels which are alike when run in one engine may vary considerably in another, it is obvious that no single laboratory procedure can be made to give results which correlate exactly with results obtained under the variety of conditions to which any motor fuel is subjected in service. Therefore the average of the road ratings obtained on each fuel during the Uniontown tests was considered the road rating of that fuel, and the laboratory method was made to result in ratings which correlated with these average road ratings.

It was found that the laboratory procedure in use prior to 1933 gave results which were generally higher than the average road ratings (11). With commercial fuels this discrepancy amounted to the equivalent of about 3 octane numbers, the maximum being 5 octane numbers. In the case of a 100 per cent experimental cracked fuel it was 9 octane numbers. By changing some of the laboratory engine operating conditions very good correlation with average road ratings was brought about, the principal changes being an increase in speed from 600 R.P.M. to 900 R.P.M., an increase in mixture temperature from approximately room temperature to 300°F., and an advance in spark timing of 3.5 degrees   These changes resulted in the present A.S.T.M. Tentative Method of Test for Knock Characteristics of Motor Fuels (Designation D 357-36T), sometimes called the motor method.

FUEL "SENSITIVITY"

Although the old procedure, now known as the research method, was displaced as a means for obtaining knock ratings for commercial purposes, it was retained for research purposes.   By rating a fuel by both methods the susceptibility of that fuel to the changes in operating conditions introduced, as compared to that of the reference fuels, can be determined.   For example, if a fuel has the same rating by both methods its knock intensity changed the same as did that of the reference fuel; if its rating differs, then the operating variables have affected its knock intensity more or less than they did the reference fuel   The difference between the ratings of a fuel obtained by the research method and the motor method has been called the "sensitivity" of that fuel (10, 2).   The data obtained in the Uniontown

tests show that those fuels having the greatest "sensitivity" as measured by the difference between the research method rating and the A.S.T.M. rating also gave the greatest differences when rated on the road. This indicates that the changes introduced in the laboratory engine operating conditions have an effect which is similar to the changes encountered in service.

Although a change in operating conditions changes the rating of a fuel, whether in the laboratory or on the road, this does not necessarily mean
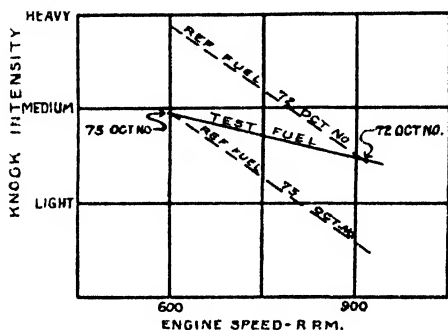
FIG 3. Effect of speed on knock intensity
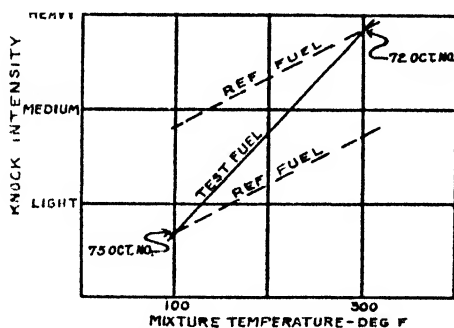
FIG 4. Effect of mixture temperature on knock intensity

that the fuel is sensitive to that change in regard to knock, for it may be the reference fuel which is sensitive. For example, from the data obtained by Campbell, Lovell, and Boyd (5) (figures 1 and 2), it appears that the change in spark timing caused no appreciable difference in the knock intensity of the cracked fuel but did considerably increase the knock intensity of the reference fuel. Therefore, in this particular case a considerable change in rating was caused by an engine variable because the reference fuel was sensitive to this variable in regard to intensity of knock,

whereas the fuel under test was comparatively insensitive. To determine whether, in general, the differences obtained in rating fuels on the road are due largely to the susceptibility of the reference fuels or of the fuels under test to the changes in operating conditions requires further investigation.

The "sensitivity" of a fuel, as defined by the difference between the research method of rating and the motor method, is determined principally by changing the engine speed and the mixture temperature of the knock-testing engine. The effect of each of these variables is shown diagrammatically in figures 3 and 4. As shown in figure 3, increasing the speed of the C. F. R. engine usually reduces the knock intensity of fuels. If a given increase in speed reduces the knock intensity of a fuel less than it does that of the reference fuel, then the rating of that fuel will be less at the higher speed than at the lower.

As indicated in figure 4, increasing the mixture temperature increases the knock intensity of fuels Therefore if a given increase in temperature produces a greater increase in the knock intensity of a fuel than it does in that of the reference fuel, the rating of the fuel will be less at the higher temperature. Therefore a fuel which rates lower by the motor method than it does by the research method may do so because it is comparatively sensitive to a change in mixture temperature and/or insensitive to a change in speed. Thus "sensitivity," as determined by the difference between the research method of rating and the A.S.T.M. or motor method, is a measure of the *relative* susceptibility of a fuel to changes in operating conditions, but is not necessarily a measure of the degree to which a fuel responds in knock intensity to such changes.

FACTORS AFFECTING LABORATORY KNOCK RATING

Since an essential factor in insuring the continued validity of the method of knock rating is the maintenance of correlation with service conditions, and since the present method was designed to correlate with the average performance in service of motor fuels in 1932 model cars, modifications in the method may be necessary from time to time because of changes occurring in motor fuels and engine designs. The road tests conducted by the C. F. R. Committee in 1934 showed that the changes made since 1932, when the method was developed, were not sufficient to warrant any modification (10). However, preliminary tests with present-day automobiles indicate that some modification in laboratory procedure is now necessary in order that knock ratings may correlate with average current service conditions. It therefore is pertinent to discuss some of the factors which might readily be changed in the laboratory procedure to produce a change in ratings.

It is well known that there are many variables which affect the knock

intensity of a fuel when burnt in an engine. Some of these are differences in design, such as combustion chamber shape or material, compression ratio, and spark plug location; others are variations in operating conditions, such as engine speed, carbon accumulation, atmospheric conditions, mixture temperature, spark advance, and mixture ratios. If these factors had the same effect on the knock intensity of all types of fuels, then they would have no effect on knock ratings. However, these factors change the knock intensity of different types of fuels in varying degrees and therefore anything which affects the detonation of a fuel may affect its rating.

Two of these factors, namely, engine speed and mixture temperature, have already been briefly discussed. Some specific data showing the effect of mixture temperature on ratings were obtained by the C. F. R. Committee (8). The fifteen fuels used in the 1934 Uniontown road tests

TABLE 2

Fuel ratings by two methods and effect of decrease in manifold temperature on octane number

FUEL	MOTOR METHOD	RESEARCH METHOD	MOTOR METHOD — RESEARCH METHOD (COLUMN 3 — COLUMN 2)	INCREASE IN OCTANE NUMBER PER 100°F. DECREASE IN MANIFOLD TEMPERATURE
1. 100 per cent cracked	70 7	79 9	9.2	2 9
2. California straight-run	71 9	73.0	1 1	0 5
3. Cracked gasoline + tetraethyl lead	74 3	78.8	4 5	2.7
4. Cracked + straight-run + lead tetraethyl	70.8	74.9	4 1	2 5
5. Cracked + straight-run	64 3	67 6	3 3	1.9

were rated by twenty laboratories at mixture temperatures of 300°F., 275°F., 250°F., and 200°F. In all other respects the procedure used was the motor method. It was found that antiknock values increase directly with decrease in manifold temperatures and that the mean antiknock value of all the fuels tested rose 2 octane numbers for each 100°F. drop in manifold temperature.

In table 2 are listed for five of the fuels tested approximately the difference between the research and the motor method ratings and the increase in octane number occasioned by a decrease of 100°F. in the manifold temperature. The maximum increase was 2.9 octane numbers for a 100°F. decrease in temperature and occurred with a 100 per cent cracked fuel which was also the most "sensitive" of all the fuels tested, as determined by the difference between the research and motor method ratings. However, the next most "sensitive" fuel gave very nearly the same decrease, al-

though the difference between the research method and motor method ratings was only slightly over one-half that of the other fuel. This perhaps indicates that the comparatively large difference between the research and motor method ratings of the first fuel was caused largely by the change in engine speed, and serves to illustrate further that the difference obtained by the two methods of rating is not necessarily indicative of the response of a fuel to a change in operating conditions.

It is a well-known fact that spark advance affects detonation, and, since the effect is dissimilar on different types of fuel, knock ratings may vary
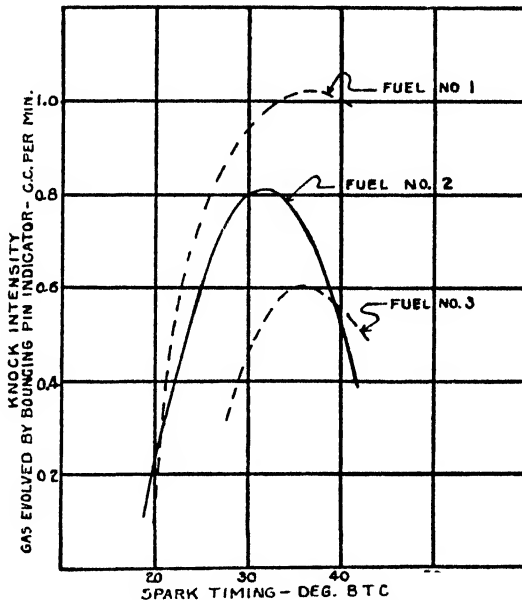
FIG. 5. Effect of spark timing on knock intensity (Campbell, Lovell and Boyd (5)).

with spark timing. Figure 5 shows the effect of spark timing on the knock intensity of three fuels. These data were obtained by Campbell, Lovell, and Boyd, using a single-cylinder engine running at 600 R.P.M. (4). It can be seen that at a 40-degree spark advance fuels 2 and 3 are alike, whereas with the spark retarded to 20 degrees before top center fuels 1 and 2 are alike. Therefore the ratings of these fuels would depend on the spark timing used.

The A.S.T.M. procedure specifies a spark timing of 26 degrees before top center when the compression ratio is 5 to 1. This timing is automatically changed with compression ratio by means of a suitable linkage. The effect of changes in this timing and its relation to maximum power and

maximum knock intensity at different compression ratios is now being studied by the C. F. R Committee.

There are many other variables which affect knock and therefore might be used to change knock ratings appreciably. However, the three discussed above, namely, engine speed, mixture temperature, and spark timing, are easily controlled and can be readily varied without necessitating any radical change in engine design or procedure. They can again be used, either singly or in combination, to effect a modification in procedure in order to obtain better correlation with average present-day road ratings. However, as pointed out above, they cannot produce exact correlation with all service conditions nor do they take care of all of the factors involved such as, for instance, the volatility and distribution effects.

Campbell, Lovell, and Boyd have presented evidence that in certain cases volatility, as well as chemical composition, may affect the knocking characteristics of a fuel (5). Because the fuel entering the cylinders of an automobile engine is only partially vaporized, the quality of the mixture delivered to different cylinders or even to any one cylinder during successive cycles is not uniform. Since the average mixture delivered by the carburetor is generally richer than that producing maximum knock intensity, it is likely that most of the knock occurring in an engine originates from the leaner charges, which are probably richer in the more volatile constituents than the original fuel If the fuel contains a comparatively large proportion of a relatively volatile fuel which is a knock suppressor, such as benzene, then the knock from these lean charges will be reduced, thus diminishing the knock produced by the engine.

In order to confirm this theory, two fuels were prepared which had the same knock rating by the A.S.T.M. method. One of these fuels was a blend of benzene and a straight-run fuel, the other was a blend of ethyl ether and a straight-run fuel. Both benzene and ethyl ether are of high volatility, and the former is a knock suppressor whereas the latter is a knock inducer. As was expected, when these fuels were compared in a car on the road, the ethyl ether blend produced a knock of light to medium intensity, whereas the benzene blend produced no knock at all, although they gave the same knock intensity when run in the single-cylinder laboratory engine where the distribution effects were not present.

FACTORS AFFECTING PRECISION OF RATINGS

There are also variables which at present are not controlled or perhaps not sufficiently so, which may affect the reproducibility of ratings. In order to determine the precision of knock ratings, a group of twenty laboratories, called the exchange group, was formed by the C. F. R. Committee. Three fuels are sent every month to each of these laboratories to

be rated. D. B. Brooks, of the National Bureau of Standards, has analyzed 1882 tests on 95 fuels made by this group for the C. F. R. Committee (3). He found the probable error of knock rating to be 0.465 octane unit. Of these 1882 tests, 86.9 per cent showed deviations from the average of less than 1 octane unit, 11.9 per cent between 1.0 and 1.9 units, 1.1 per cent between 2.0 and 2.9 units, and 0.1 per cent over 2.9 units. The types of fuels used were as follows: straight-run fuel with and without lead tetraethyl; aviation fuel with and without lead tetraethyl; straight-run fuel plus cracked fuel; straight-run fuel plus cracked fuel with lead tetraethyl; 100 per cent cracked fuel; two benzene blends; two reference fuels. Of these the 100 per cent cracked fuel showed a distinctly larger error than the others.

The two reference fuels were sent out as test fuels and so were rated against themselves without the knowledge of the operator. Therefore any errors obtained with these fuels were due to experimental errors rather

TABLE 3

Change in octane number for carbon accumulation due to 100-hour operation

FUEL	AVERAGE CHANGE	GREATEST CHANGE	
Straight-run (plus lead tetraethyl)	+0 05	+2 0	−0 8
Straight-run (plus cracked)	−0.3	+0.1	−1.2
Straight-run cracked + lead tetraethyl	−0.8	+1 1	−1.2
100 per cent cracked	−1 2	+0 1	−2.6

than variations in conditions. If the ratings of these two fuels are assumed to be representative, then perfect technique would reduce the probable error from 0.465 to about 0.25 octane unit.

The factors, other than experimental error, to which these deviations were attributed, were humidity, knock intensity, and carbon accumulation.

The effect of carbon accumulation as determined by these tests is presented in table 3. These data indicate that fuels containing cracked gasoline respond to carbon accumulation, showing a lower octane number on engines run over one hundred hours without cleaning than do the other types of fuel.

It is well known that humidity affects detonation, increasing humidity decreasing the knock. Its effect on knock ratings is being studied by the C. F. R. Committee, and the results of some tests to determine this effect have been reported by J. R. MacGregor (9). He found that the reduction in knock intensity for a given increase in humidity was approximately the same for a straight-run, secondary reference fuel blend, a benzene blend, and a cracked fuel, all of about 68 octane number. Thus a change in

humidity would not affect the rating of these fuels when matched against the secondary reference fuels. However, the effect on knock intensity of an increase in humidity was considerably less with a blend of 67.5 per cent octane and 32.5 per cent heptane and considerably more with a straight-run secondary reference fuel blend containing 2.2 cc. of lead tetraethyl. Thus, if octane–heptane blends were used as reference fuels, the ratings of all the other fuels would be affected. An increase in humidity from 0.002 to 0.023 lb. of water per pound of dry air was estimated to affect the leaded reference fuel approximately 5.7 octane units when matched against octane–heptane blends, and 3.6 octane units when matched against the unleaded secondary reference fuels.

In order to determine whether more rigid specifications regarding the knock intensity at which to rate fuels would result in improved precision, the C. F. R. Committee is also investigating this factor. At present, this is specified in the procedure by prescribing that a rating should be made at one compression ratio higher than that producing incipient knock, which should result in a knock intensity equivalent to that obtained by a 65 per cent blend of isooctane in 35 per cent normal heptane with the engine set at 5.3 to 1 compression ratio at a barometric pressure of 29.92 in. of mercury (1). Since it is difficult to determine incipient detonation exactly, particularly where other noises are present, and its reproducibility is open to question, the more definite secondary specification has in practice largely superseded the one based on incipient knock.

The results of some tests conducted by the C. F. R. Committee on the effect of knock intensity on ratings were reported by Neil MacCoull (7). For these tests the following fuels were used: a blend of benzene in reference fuel C-9, a commercial gasoline containing at least 0.7 cc. of lead tetraethyl per gallon, and two stabilized, highly cracked gasolines from different sources. These four fuels were rated by the nineteen member laboratories of the exchange group at two compression ratios, one 0.2 of a ratio higher than standard and one 0.2 of a ratio lower than standard. Otherwise, the method used was identical with the A.S.T.M. procedure. The results obtained indicated that increasing the compression ratio increases the knock rating, but, as might be expected, the amount of increase varies with the type of fuel. Thus the maximum increase of the average ratings of all the laboratories occurred with the benzene blend and equalled 2.2 octane numbers. The minimum increase was 0.3 octane number with the commercial fuel. The two cracked fuels gave a difference of 1.1 and 1.2 octane numbers. These differences are not very great, considering that the difference in knock intensity used was appreciable, namely, that produced by a difference in compression ratio of 0.4, whereas the standard knock intensity is such that a reduction of 1 in the compression ratio would reduce the intensity to zero.

In conclusion it may be said that, through the coöperative efforts of members of both the petroleum and automotive industries, a great deal of work, of which only a small part could be taken up within the limits of this paper, has been and still is being done towards establishing a precise means of evaluating the knock characteristics of motor fuels. It is to be hoped that the many factors regarding detonation brought out as a result of this work will also aid in shedding more light on this complex phenomenon of combustion.

REFERENCES

(1) A S. T M. Standards on Petroleum Products and Lubricants, Designation D357-36T

(2) BROOKS, DONALD B : S A E Journal **32**, No 5, May, 1933.

(3) BROOKS, DONALD B : S A E Journal **39**, No 4, October, 1936.

(4) CAMPBELL, J M., LOVELL, W. C , AND BOYD, T. A : S A. E Transactions **26**, 459 (1931)

(5) CAMPBELL, J. M , LOVELL, W G , AND BOYD, T. A : S. A. E. Journal **40**, No. 4, April, 1937.

(6) EDGAR, G : S. A E. Transactions **22**, Part 1 (1927).

(7) MACCOULL, N.: The Effect of Knock Intensity on Fuel Knock Ratings; presented at the Annual Meeting of the Society of Automotive Engineers, January, 1937

(8) MACCOULL, N , EDGAR, G , AND BARNARD, D. P.: Proc. Am. Petroleum Inst., 5th Mid-Year Meeting, Section III on Refining, p. 89 (1935).

(9) MACGREGOR, J. R.: S A. E Journal **40**, No. 6, June, 1937

(10) VEAL, C B : C. F. R Committee Report on 1934 Detonation Tests, S. A. E. Transactions **30**, 165 (1935).

(11) VEAL, C. B , BEST, H. W., CAMPBELL, J. M., AND HOLADAY, W. M.: S. A. E. Transactions **28**, 105 (1933)

DISCUSSION[1,2]

BERNARD LEWIS AND GUENTHER VON ELBE: It should be possible to interpret the experience in the road service tests mentioned by Mr. Best by a consideration of the ignition regions and ignition lag periods of various types of fuels.

Knocking is avoided if the flame travels throughout the combustion space of the engine in a time which is shorter than the ignition lag time of the last part of the charge to burn. The ignition lag of a given fuel-air mixture is, among other factors, a function of temperature and pressure. The lower part of the accompanying figure contains typical curves of equal ignition lags in a temperature–pressure diagram (Townend). The actual

position of these curves is influenced by engine design, but some such set will be valid for a given engine. Keeping the spark timing constant and assuming constant intake pressure and mixture composition, we shall confine ourselves mainly to the variation of the temperature of the compressed unburned charge with engine speed. This relation depends on design factors. It will be assumed that the temperature increases somewhat with engine speed, as shown in the upper part of the figure. Measurements on a C. F. R. engine have shown that the temperature goes through a maxi-
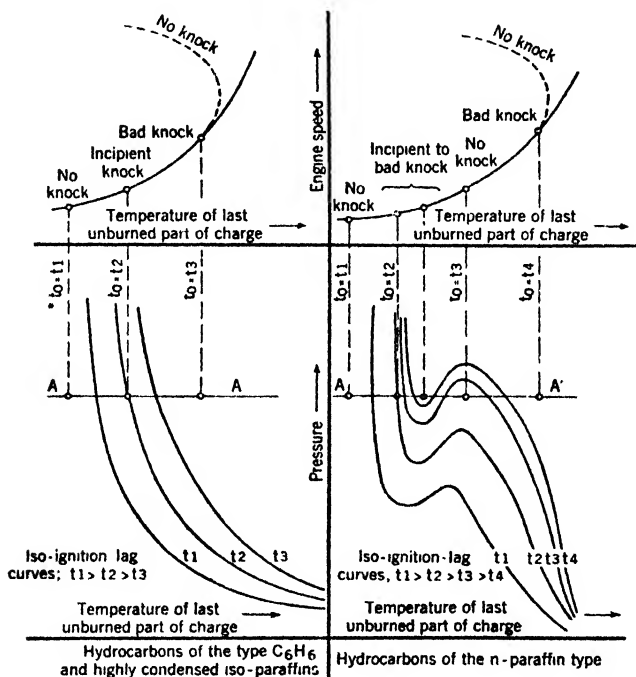
Fig. 1. Relation between knock, fuel, and engine speed t_0 = time required for normal combustion.

mum (Seeber: Dissertation, Breslau, 1932; see also Philippovich: Z. Elektrochem. **42**, 472 (1936)). While we have no further knowledge of this relation, the assumed dependence in the upper part of the figure will suffice to illustrate the possibilities of explaining the observed relationships between engine speed and knock.

Let us, for example, take the experience of service tests that a cracked fuel showed one region of knock at high speeds and a straight-run fuel two regions of knock, one at low and the other at high speeds. The behavior of the cracked fuel may be understood from the left-hand side of the figure.

Let us assume that a pressure corresponding to the line AA' is reached in the last part of the charge. As the engine speed increases the temperature increases and the time, t_0, required for normal combustion decreases (probably mainly owing to turbulence). Three iso-ignition-lag curves are shown with lag periods corresponding to $t_1 > t_2 > t_3$. If $t_0 = t_1$ at the temperature shown, the flame will travel throughout the combustion space in a time shorter than the ignition lag and no knock will result. When, on increasing the engine speed, $t_0 = t_2$ at the temperature shown, there will be incipient knock, since the time of flame travel is just equal to the ignition lag. On further increase of the engine speed, the time required for normal combustion becomes longer than the ignition lag, the discrepancy increasing with engine speed, resulting in an increase in the severity of the knock. If the temperature–engine speed curve goes through a maximum, the knock will decrease again in severity and finally disappear. By the same procedure, it is easily seen that straight-run fuels which have the peculiar peninsula-shaped iso-ignition-lag curves shown in the right side of the figure should exhibit two knocking regions, one at low and the other at high speed.

Changes in spark timing shift the line AA' to other positions and change the position of knock with respect to engine speed accordingly, spark advance increasing the knocking tendency and spark retard decreasing it.

Although the foregoing outline is admittedly crude, it nevertheless is suggestive of the direction in which future research might move in order to find improved methods of rating fuels. The crux of the problem is the separation of pure fuel factors and engine factors. Although the present analysis is partly hypothetical, it is not impossible that it accomplishes this separation to a satisfactory degree. It need only be assumed that the iso-ignition-lag curves are not very different in engines of the same type. This is a matter for experimental test. If this is so, then the lower part of the figure represents essentially fuel characteristics and the upper part engine characteristics. Fuel rating would then consist, in principle, in the determination of iso-ignition-lag curves. The sets of curves for two given fuels may actually cross each other. Since that fuel is better whose ignition lag curves lie farthest to the right in the figure, it is evident that fuel A may be superior to fuel B under one set of engine conditions, and inferior under another set of engine conditions. Having established the engine characteristics as is shown, for example, in the upper part of the figure, it should become possible to predict the better fuel under various service conditions.

F. L. GASTON (Shell Petroleum Corporation, St. Louis, Missouri):[*]
Mr. Best makes the statement that the sensitivity of a fuel does not neces-

sarily indicate the response in knock intensity to any variable. One of the difficulties of engine research is that a change in one variable frequently causes an unavoidable change in another, and hence the various factors involved often cannot be studied one at a time.

The research method minus motor method sensitivity involves sensitivity to air intake temperature, to jacket temperature, and to speed. In some experiments which we made some time ago, the sensitivity to jacket temperature was found to be nearly twice as great as the sensitivity to intake temperature. However, raising the intake temperature reduces the weight of air drawn into the cylinder on each stroke and hence the tendency to detonation. When the results were corrected to the same volumetric efficiency, it was found that intake temperature was more effective in reducing the knock rating of temperature-sensitive fuels than a similar increase in jacket temperature, as one would expect.

MOLECULAR STRUCTURE OF HYDROCARBONS AND ENGINE KNOCK

WHEELER G. LOVELL AND JOHN M. CAMPBELL

Research Laboratories Division, General Motors Corporation, Detroit, Michigan

During the past ten years considerable progress has been made in the development of a knowledge of the relationship between molecular structure and knocking characteristics of hydrocarbons when used as fuels in internal-combustion engines (1 to 22). This knowledge is of considerable significance both from the engineering standpoint, where power output or thermal efficiency is a primary consideration, and also from a more theoretical standpoint, where it is desired to extend our present understanding of fuels and combustion reactions.

From the engineering standpoint, it will suffice here to point out that the efficiency of the conventional internal-combustion engine is largely dependent upon compression ratio,—increasing compression ratio making possible higher efficiency and greater power output per unit of engine displacement. Thus, within certain limits, it is desirable to use a high compression ratio, but the limit to which it is possible to go is determined by the tendency of the fuel to knock. This is a very real limitation, and that it is intimately related to the subject of molecular structure is shown by the fact that the maximum power output obtainable without knock from an engine of given piston displacement may vary by as much as 50 per cent with different isomeric paraffin hydrocarbons. Needless to say, the further development of knowledge in this direction is almost certain to have an important and far-reaching influence in the engineering progress of the automobile, aviation, and petroleum-refining industries.

The unique feature of this general situation is that the still largely unknown phenomena of gaseous combustion in an engine are controlled by slight differences in the molecular structure of fuels to an extent of tremendous economic importance. We know that the structures now predominant in most commercial fuels are relatively very poor as compared with those that we would have, had we better control of chemical reactions such as those of isomerization. This situation represents a common meeting ground of molecular physics, gaseous combustion, organic chemistry, and economics of considerable social importance.

For the purposes of this symposium we are mainly concerned with what might be termed the theoretical standpoint. Certainly the observations which have thus far been made in connection with this subject provide material which can be woven into the theory of many branches of science to give, eventually, a clearer conception of the mechanisms involved. It will be a purpose of this paper to review some of the consistent relationships between molecular structure and knock which have been found.

It now appears that chemical constitution, as revealed by molecular structure, is related to knock, and hence the ultimate utility of a fuel, in two distinct ways. first, by direct influence on knock, and second, by influencing the effectiveness of antiknock compounds when used in the fuels.

In order to evaluate the relationship between the structure of hydrocarbons and their tendency to knock, various methods have been used, all of them depending upon direct measurements in an engine. The use of an engine is essential, since we do not have precise enough information as to the conditions in an engine cylinder to enable them to be duplicated satisfactorily or conveniently outside of an engine. However, it happens that an engine under the proper conditions offers an extraordinarily sensitive, convenient, and rapid method of measurement. The development of the concept of the octane number of a fuel, and of the standardized method of its measurement, discussed in detail elsewhere in this symposium, is a specific application of this principle to the testing of commercial gasolines. This commercial testing method, because of the restricted engine conditions employed in it, is not ideally adapted to the broad study of the knocking characteristics of hydrocarbons. Consequently, in the work described herein, wide deviations from the commercial test procedure have been utilized.

One method of measurement which has been used with hydrocarbons is to burn the hydrocarbon in question as a fuel in an engine in the pure state and to determine the maximum compression ratio at which it will operate without knock. This method is quite simple and direct, although the values must, of necessity, relate to the particular engine and operating conditions used in the experiments. For some purposes this method is not entirely suitable, because the materials under test may not have physical properties adapted for use in a carburetor. It also has another disadvantage in that the use of that method of measurement requires considerable amounts of material for test, and such amounts may not always be available in the case of compounds whose laboratory preparation is difficult.

For these and other reasons measurements have often been made in solution in a reference or standard fuel, measuring the change in knock of

the fuel upon the addition to the fuel of a definite amount of the material under test.   The change in knocking behavior may be conveniently expressed as the change in the equivalent octane number of the fuel or, as was done before this method came into use, it may be measured and expressed in terms of the amount of an antiknock compound such as aniline or lead tetraethyl which will produce a similar change in knocking tendency. Other modifications of these most widely used methods have been used; for a complete discussion of them and the precise methods of test and computation, reference may be made to the original papers.

As previously mentioned, all methods involve the use of an engine, and it is true that the precise values obtained will depend to an extent upon the engine used and the conditions under which it is operated.   In other words, the knocking characteristics of a fuel are not entirely a property of the fuel alone.   From the limited amount of data thus far made available, it appears that, with few exceptions, the changes in the values of different hydrocarbons observed under different engine conditions are relatively small as compared with some of the differences between different hydrocarbons under comparable engine conditions.   Again, for detailed expositions of these phenomena reference must be made to separate papers covering these various aspects of the subject (5, 7, 15).

It is of considerable significance, however, that under given engine conditions the knocking characteristics of hydrocarbons fall into a very consistent pattern, according to their molecular structure.   The significance of this may be twofold.   This consistent behavior enables one to make an appraisal of what the possibilities are in the way of fuels whose thermodynamic efficiency in an engine may be very high, or of what efficiencies are possible when the present barriers of lack of knowledge as to chemical conversions are removed or reduced.   This consistent behavior may also serve as a guide in evaluating theories of the mechanism of hydrocarbon combustion and the incidence of knock in engines.   For these reasons it may be valuable in a symposium of this type to review these consistencies, in order that the facts upon which theories or predictions may be based may be clearly in mind.

It is convenient for the sake of simplicity to consider the hydrocarbons in classes, such as paraffins, olefins, etc., and the relationships are most readily expressed graphically.   Figure 1 summarizes the relationships for the paraffin hydrocarbons.   The knocking characteristics are expressed in terms of "aniline equivalent," which is a measure of the knocking behavior in relatively dilute solution in which concentrations are on the basis of the same number of molecules (12).   In order, however, to convey some concept of the scale of aniline equivalent, it may be said that n-heptane with an aniline equivalent of -14 and 2,2,4-trimethylpentane, which has a

value of $+16$, begin to knock when burned undiluted at compression ratios of 2.7 and 6.9, respectively. While such values do not permit a direct conversion of all values, because the relative values obtained in dilute solution with gasoline are not necessarily an index to behavior in the undiluted state, nevertheless they do give an idea of the great range covered by the vertical scale.

FIG. 1 Relationship of molecular structure to knocking characteristics of paraffin hydrocarbons

From this diagrammatic representation it may be seen that in a very general, and consistent way the addition of methyl groups improves the molecule from a knock standpoint; lengthening the straight chain of a molecule makes the knocking characteristics worse, and centralizing the molecule, without changing the number of atoms, makes a much better

molecule as far as knock is concerned.   On this molecular basis it is a fair approximation to say that the knock depends roughly upon the length of the unbranched straight chain of carbon atoms in the molecule.   This is a fact that is probably of considerable significance as far as theories of the mechanism of combustion and knock are concerned.
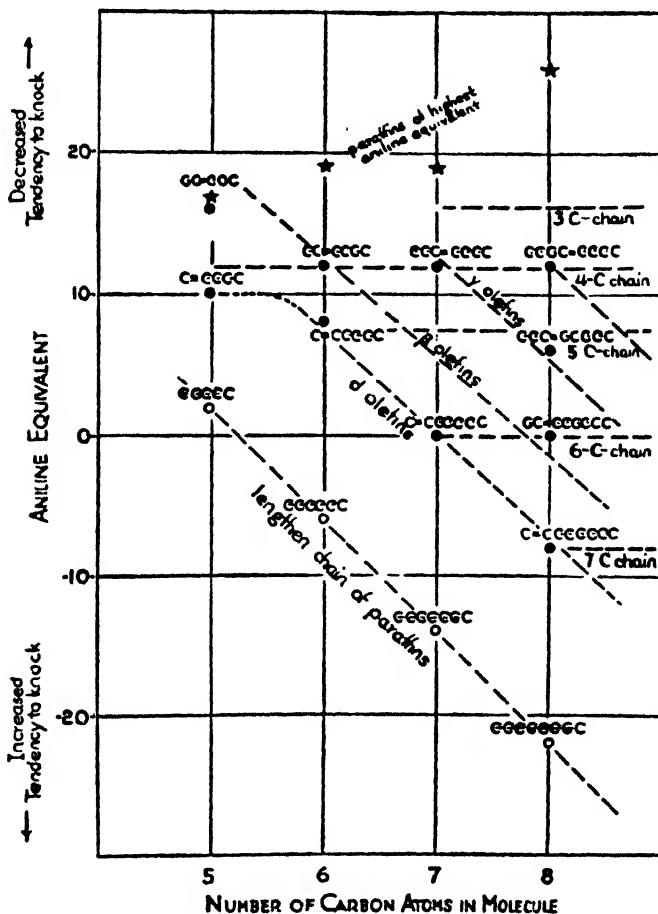
FIG. 2. Knocking characteristics of straight-chain olefins

This same behavior is also exhibited by the straight-chain olefin hydrocarbons, whose properties in this regard are represented graphically in figure 2 (13).   The effect of an increase in the straight paraffin chain is similar, both qualitatively and quantitatively, to that observed in the case of the paraffin hydrocarbons.   It is also probably significant that,

within the range covered, the knock seems to depend upon the length of the straight paraffin chain, irrespective of the size of the molecule.

Branched-chain olefins behave very much as might be expected from what might be termed the effect of the double bond, as revealed by the straight-chain olefins, combined with the effect of branching, as shown by
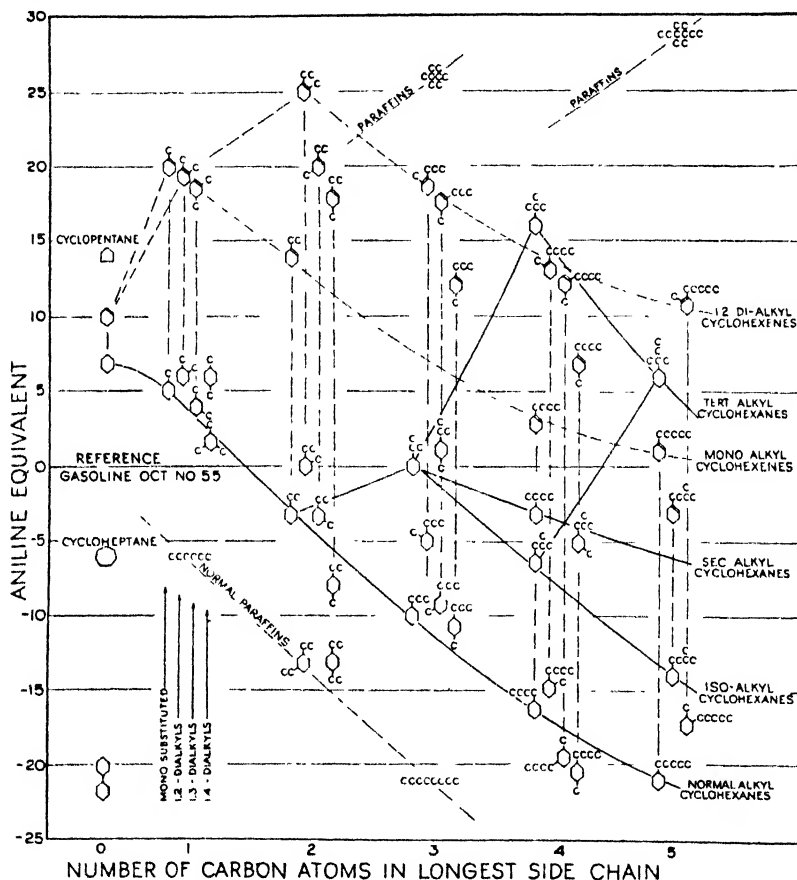
FIG. 3. Relative knocking characteristics of alkyl cyclohexanes and cyclohexenes

the behavior of the paraffins. The great numbers of isomers of such compounds, however, make the obtaining of a complete picture of their behavior a very difficult and tedious matter.

Another class of hydrocarbons is that of those containing a cyclopentane or a cyclohexane ring (14). In general the formation of a ring, as indicated by the behavior of cyclopentane, cyclohexane, and cycloheptane, is to

enhance the degree of freedom from knock of the compound as compared with the paraffin containing the corresponding number of carbon atoms. The possibilities of isomerization in this class of compound are somewhat different from those in the aliphatic compounds, although the effect of changes in the arrangement of an alkyl side chain is similar to that which might be expected by analogy with the paraffin hydrocarbons. This is shown by the graphical representation of the data on the cyclohexanes and cyclohexenes in figure 3, plotted in a manner similar to the preceding data. The possibilities of isomerism due to variations in the positions of two or more side chains have not seemed to be a relatively great factor in determining knock. However, the available data do seem to indicate that, as far as isomerism with respect to a different distribution of carbon atoms between chains is concerned, the most favorable condition from the standpoint of knock prevails with the most centralized structure. If we should define such a rough concept as centralization by a compact arrangement of the plane structural formula ordinarily used, this generalization seems to apply quite generally to all types of compounds investigated. It is also interesting in connection with these cyclic compounds that an introduction of a double bond in the ring increases the freedom from knock of the compound by an amount which seems quite constant.

Cyclopentanes and cyclopentenes seem to behave, as far as their knocking characteristics are concerned, in a manner quite analogous to that of the six-membered rings.

Another class of hydrocarbons of considerable interest in connection with the problem of knock is that of the aromatic compounds containing a single benzene ring (15). Data on these are represented graphically in figure 4. The behavior of these compounds is different from that of the naphthenes as far as the effect of an increasing length of side chain is concerned. The addition of a side chain and its progressive lengthening first results in an increase in freedom from knock; further lengthening of the chain results in a decrease. While this peculiarity might suggest some analogy to be expected with the behavior of these compounds on oxidation, at present this is largely speculative. The effect of the initial methyl substituents, however, is very pronounced, as toluene is much better than benzene, and the xylenes and mesitylene are still better; the effect of position isomerism seems to be a large factor. The aromatic compounds behave with respect to knock as if the benzene ring were of paramount importance and as if the addition of one or more carbon atoms to it were of much greater effect than the arrangement of the atoms within the chain which is added. Most of the aromatic compounds are relatively good from the standpoint of knock as compared with the other conventional classes of hydrocarbons; it is, however, quite difficult if not impossible to assign

relative values to these classes as a whole, since the range covered by the different classes is widely, if not almost completely, overlapping.

The relationships just discussed relate to dilute solutions and are upon a molecular basis; they are of primary interest because of the suggestive consistencies of the correlations between knock and structure. From the standpoint of the fuel and the engine they are of particular interest,
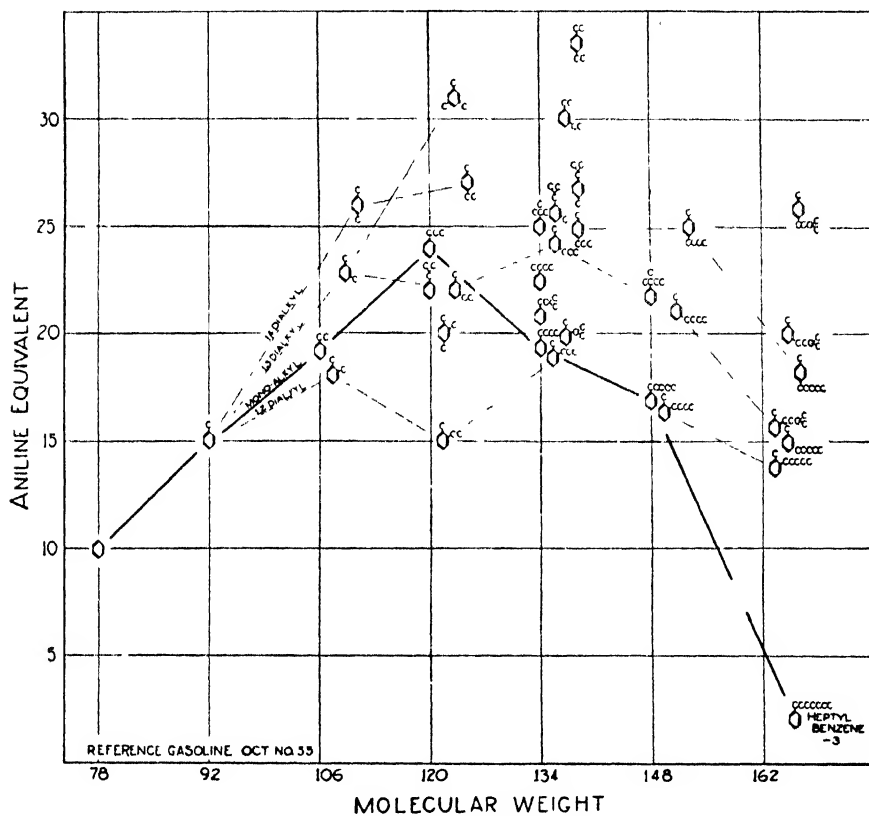
FIG. 4. Relative knocking characteristics of aromatic hydrocarbons

as indicating what may be obtained in practice from relatively small additions of different hydrocarbons in making up fuels better than those now commercially available and with a fairly wide range of constituents.

From the standpoint of making large advances in fuel technology, the knocking behavior of individual hydrocarbons in the pure state is of special importance. Considerable data are available on pure hydrocarbons in terms of the compression ratios that may be used with them, although of

necessity, as previously mentioned, they are of more limited extent.   The general qualitative correlations between knocking characteristics and molecular structure previously observed for such hydrocarbons when measured in dilute solutions hold in general, but there are some notable exceptions.   These arise from the fact that the critical compression ratio of a mixture of two compounds is not always directly proportional to the concentration of each in the mixture.   There is also another contributing factor which will be discussed later, namely, that the engine operating con-
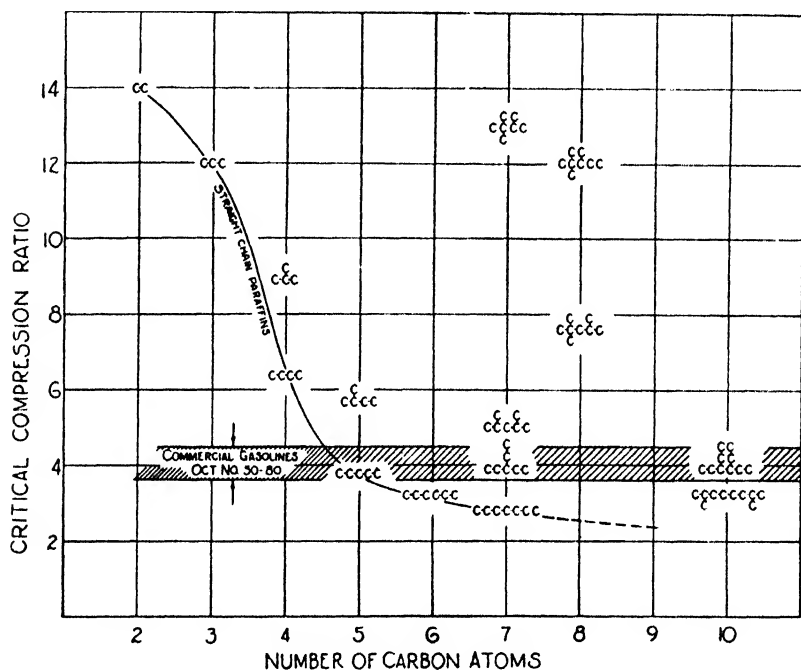
Fig. 5. Critical compression ratios of paraffin hydrocarbons

ditions make a considerable difference in the relative values obtained for some fuels when they are tested in the pure state.

However, a general picture of the relationships among the paraffin hydrocarbons is shown in figure 5, where the knocking characteristics of the pure paraffin hydrocarbons are evaluated in terms of the critical compression ratio or the highest ratio at which they can be used without knocking (16).   Most apparent, of course, are the very great differences between the different compounds.

A similar picture for the cyclic compounds is shown in figure 6.   Outstanding here are the very great differences between the aromatic com-
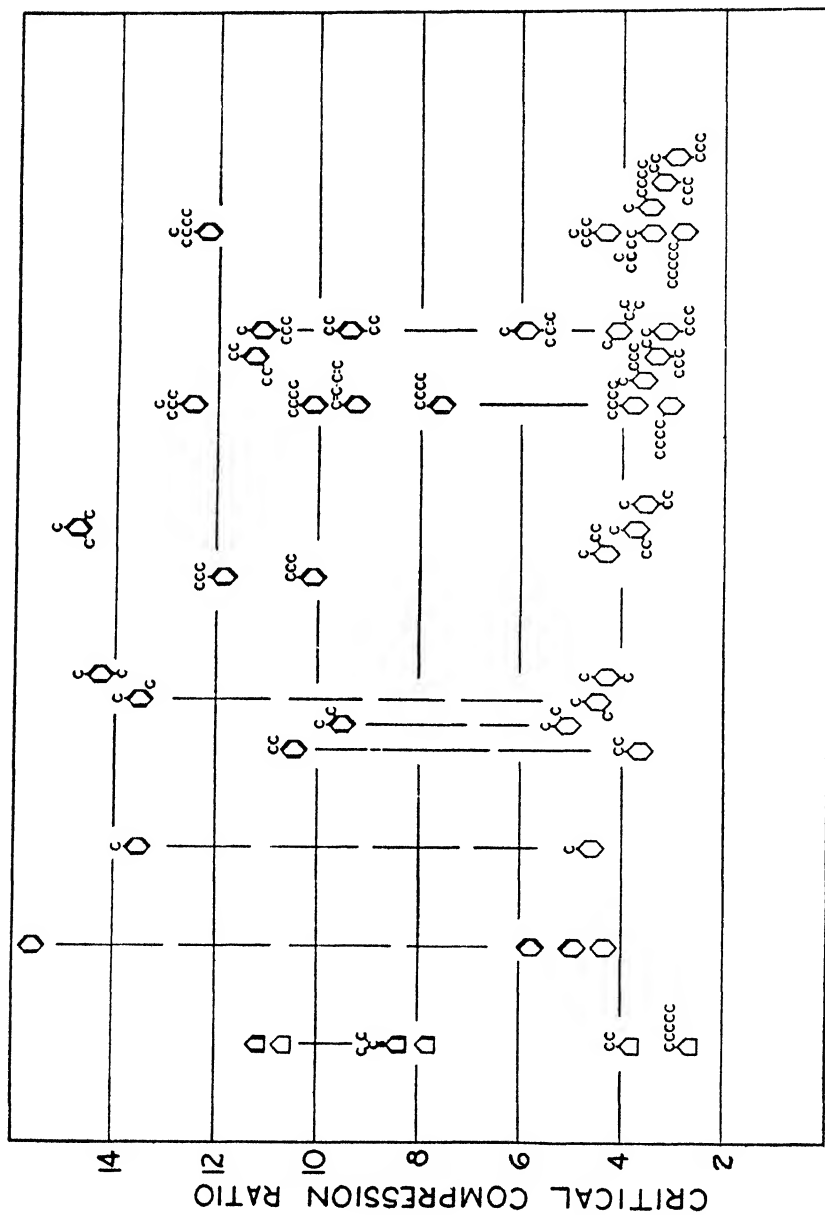
Fig. 6. Comparison of benzene and cyclohexane derivatives

pounds and the corresponding saturated compounds, a phenomenon which does not appear with measurements made under conditions of dilute solutions. The knocking tendency of a mixture is not necessarily a linear function of the concentration. This behavior is shown by the data of figure 7, in which the critical compression ratio of some two-component mixtures is plotted against the mole fraction in the solution. The curves are not linear and show a wide variety of characteristics, some being convex and some concave downward. In general, extrapolation of knock–con-
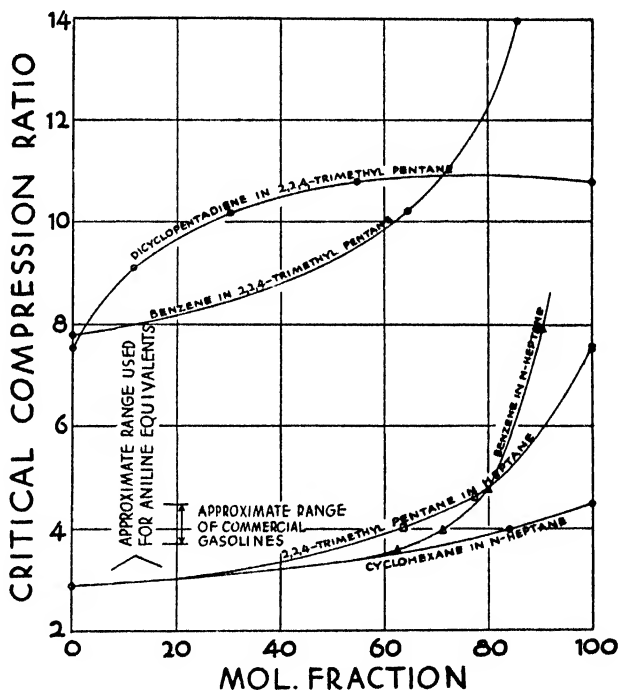
FIG. 7. Knocking characteristics of two-component hydrocarbon mixtures

centration curves over a considerable range is not justified. The reasons for these departures from mere simple relationships are of considerable speculative interest, but our present knowledge of hydrocarbon combustion is possibly too limited to warrant extensive discussion of this here.

The relationships among hydrocarbons with respect to knock and utility are also of interest from the viewpoint of the mechanism of combustion, because of the way in which antiknock compounds act upon them (3, 5, 6). The mechanism of antiknock action seems to be tied up with the molecular structure of the hydrocarbon, probably as a result of the intermediate

compounds formed. In some compounds lead tetraethyl, for instance, may be twenty times as effective as a knock suppressor as in others; in some compounds it may even be a knock inducer.

As an index of this effectiveness, we may consider the increase in critical compression ratio which the addition of 1 cc. of lead tetraethyl will permit. It is possible to correlate such values upon the basis of the branching of carbon chains, upon the position of double bonds in a chain or in a ring, and so on. These manifold and consistent relationships may not well be detailed here. However, as a rough general correlation, the data shown
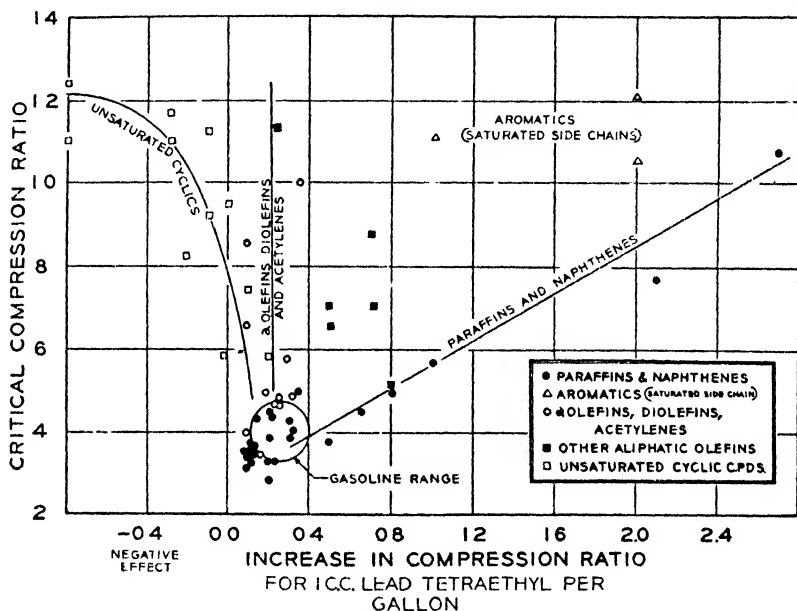
FIG 8. Relative antiknock effect of lead tetraethyl in various types of hydrocarbons

graphically in figure 8 indicate the extent of the variation, since the addition of 1 cc. of lead tetraethyl to a hydrocarbon may permit an increase of 2.7 ratios without knock, or may necessitate a decrease of 0.8 of a compression ratio. As a single example of how specific this effect is, there are the data of figure 9, which are self-explanatory. Since any consistent theory of knock must include the action of antiknock compounds, it is important to note that some antiknock compounds or catalysts may under some circumstances act as knock-inducing compounds.

An evaluation of the relative utilities of fuels of different molecular structures is essentially a measurement of the thermodynamic efficiency

with which each may be burned in an engine suited to that particular fuel. As mentioned previously, this is a property not entirely of the fuel but also of the engine; the engine must to a considerable extent be adapted to the fuel in other respects than simply in regard to the compression ratio.

A concept of why this comes about may be readily gained by thinking of the phenomenon of knock as essentially a race between two combustion processes in the engine cylinder. The first is the spread of flame across the cylinder; the second is the series of steps leading up to ignition of the fuel–air mixture ahead of the flame. Which phenomenon takes place first determines whether or not there is knock. Both processes are influenced
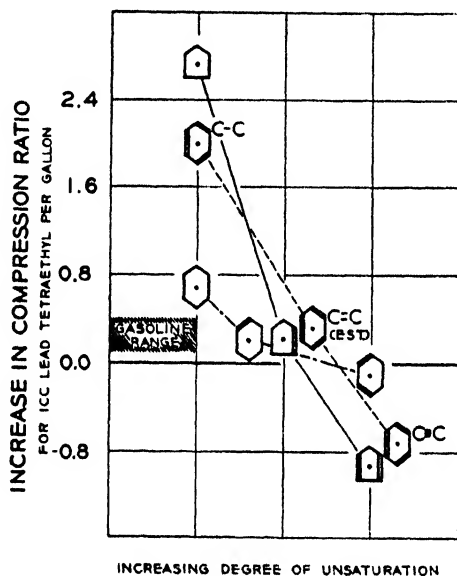
FIG. 9. Effect of double bonds in cyclic compounds on effectiveness of lead tetraethyl

by the time available, by temperature, and by pressure, so that the outcome of the race will depend upon such conditions. Furthermore, the extent to which these different processes are affected by temperature and pressure will vary from one hydrocarbon fuel to another. It is to be expected, consequently, that the attainment of the greatest efficiency is to be had only by the best fitting together of fuel and engine. This amounts to selecting a raw material (fuel) and carrying out a chemical reaction on it (combustion with air) under conditions best adapted to secure the greatest yield of work with it. The selection of the initial fuel material is influenced, first, by the relative ease with which it may be made from petroleum or

other raw material, and, second, by the conditions which it requires for its best combustion.

The first factor, that of the preparation of the fuel from petroleum or other sources of raw material, is dealt with in other papers of this symposium; the conditions for best combustion may be outlined here so as to show some of the controlling conditions influencing the selection of fuels.
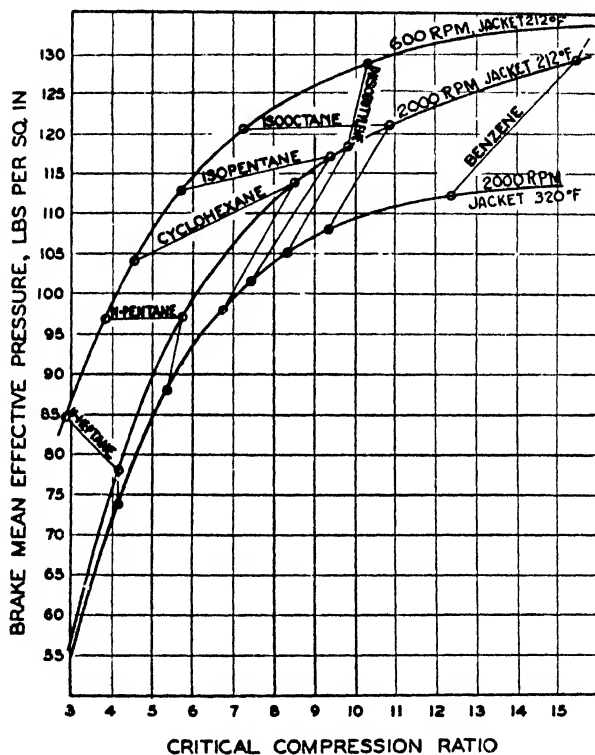
FIG 10. Power characteristics of a $3\frac{1}{4}$ in. x $4\frac{1}{2}$ in. single-cylinder, variable-compression engine. Mixture ratio and spark timing for maximum power. Mixture temperature approximately 60°F.

As is well known, the compression ratio gives a fair index of the relative thermodynamic efficiency of combustion, if and only if other factors are kept constant. The numerical values of compression ratio so obtained, however, are quite without absolute significance, except as they pertain to the particular conditions utilized. An evaluation of such a scale is figure 10, where, taking the data from one variable compression engine, brake mean effective pressures are plotted against the compression ratios at which the engine was operated. Spotted along the curve are a number of

points which represent the highest compression ratio at which the hydrocarbons indicated may be used without knock, under the particular conditions of the tests. Three such curves are shown, representing different engine speeds and different temperatures of the cylinder jacket. It is obvious from the three curves that with different fuels there are very great differences between the efficiencies or power outputs possible with knock-free operation.

Equally important are the changes in the relative behavior of different hydrocarbons when burned in an engine under different operating conditions. The paraffins and cyclohexane decreased in knocking tendency as the speed was increased. Diisobutylene, an olefin, knocked more with increasing speed, as shown by the lowering of the critical compression ratio with increased speed. Increasing the jacket temperature resulted in general in an increase in knocking tendency, although the change varied greatly from one fuel to another.

The comparison between isooctane and diisobutylene is of particular interest because it illustrates the differences in knocking characteristics, as affected by engine conditions, that may exist between an olefin and the corresponding paraffin. At 600 R.P.M. diisobutylene has much less tendency to knock than isooctane under the engine conditions represented in figure 10. But at 2000 R.P.M. the relative knocking tendencies of these two hydrocarbons are completely reversed and the saturated paraffin, isooctane (2,2,4-trimethylpentane), becomes the superior fuel.

These data indicate that the relative knocking tendencies of different hydrocarbons may be expected to be affected to a considerable degree by changes in engine conditions. Consequently the choice of fuel and engine conditions to be used for the production of maximum output involves an evaluation of the relative effects of a number of different variables, of which only two of the more outstanding ones—engine speed and jacket temperature—have been discussed herein.

REFERENCES

(1) BIRCH, S. F., AND STANSFIELD, R.: Nature **123**, 490 (1929).
(2) BIRCH, S. F., AND STANSFIELD, R.: Nature **123**, 639 (1929).
(3) CAMPBELL, J. M , SIGNAIGO, F K., LOVELL, W. G., AND BOYD, T. A.: Ind. Eng. Chem. **27**, 593 (1935).
(4) EGLOFF, G.: Natl. Petroleum News **28**, No. 42, 25 (1936).
(5) GARNER, F. H., AND EVANS, E. B.: J. Inst. Petroleum Tech. **18**, 751 (1932).
(6) GARNER, F. H., WILKENSON, R., AND NASH, A. W.: J. Soc. Chem. Ind. **51**, 265T (1932).
(7) GARNER, F. H., EVANS, E. B., SPRAKE, C. H., AND BOOM, W. E. S.: Proc. World Petroleum Congr. II, 170 (1933).
(8) HOFFMAN, F., LANG, K. F., BEBLIN, K., AND SCHMIDT, A. W.: Brennstoff-Chem. **13**, 161 (1932).

(9) HOFFMAN, F., LANG, K F., BERLIN, K., AND SCHMIDT, A. W.: Brennstoff-Chem. **14**, 103 (1933)

(10) HOWES, D A , AND NASH, A. W : J. Soc. Chem. Ind. **49**, 16T (1930).

(11) HOWES, D. A , AND NASH, A. W.: J. Soc. Chem. Ind. **49**, 113T (1930).

(12) LOVELL, W G , CAMPBELL, J. M , AND BOYD, T. A.: Ind. Eng. Chem. **23**, 26 (1931)

(13) LOVELL, W G , CAMPBELL, J. M., AND BOYD, T A : Ind. Eng. Chem. **23**, 555 (1931)

(14) LOVELL, W. G , CAMPBELL, J M., AND BOYD, T. A.: Ind. Eng. Chem. **25**, 1107 (1933)

(15) LOVELL, W G , CAMPBELL, J M , SIGNAIGO, F. K., AND BOYD, T A.: Ind. Eng. Chem **26**, 475 (1934)

(16) LOVELL, W G., CAMPBELL, J. M , AND BOYD, T A.: Ind. Eng. Chem. **26**, 1105 (1934).

(17) NASH, A W , AND HOWES, D. A.: Nature **123**, 276 (1929).

(18) NASH, A. W , AND HOWES, D. A.: Nature **123**, 526 (1929).

(19) NEPTUNE, F B., AND TRIMBLE, H. A : Oil Gas J. **32**, No. 51, 44 (1934).

(20) SCHMIDT, A W : Petroleum Z. **28**, March 9, Motorenbetrub, p. 2 (1932).

(21) SCHMIDT, A. W.: Angew. Chem **44**, 476 (1931).

(22) THORNYCROFT, O., AND FERGUSON, A : J. Inst. Petroleum Tech **18**, 329 (1932).

FUELS FOR INTERNAL-COMBUSTION ENGINES

GUSTAV EGLOFF, W. H HUBNER, AND P. M. VAN ARSDELL

Research Laboratories, Universal Oil Products Co , Chicago, Illinois

CONTENTS

I. INTRODUCTION

The volume of motor fuels available is an astronomical figure.   At the present time motor fuels are produced primarily from crude oil, natural gas, and coal   The fuels are derivable from gases such as methane, ethane, propane, and butanes of octane numbers from 90 to 125, from fuels produced from the polymerization of gaseous olefins and paraffinic hydrocarbons of octane ratings from 75 to 100, and from alcohols, isopropyl ether, or mixed ethers and ketones of high octane numbers.   As a comparison, natural gasolines have octane ratings of from 70 to over 80, and the octane ratings of gasolines from the atmospheric distillation of crude oils vary between 15 and 70, while cracked gasolines have antiknock values ranging between 60 and 80 octane.   The gaseous motor fuels can also be produced from gases obtained from the cracking process as well as from natural gas.   Cracked or natural gases can be converted into high-octane liquid motor fuels by the thermal or catalytic polymerization processes. Motor fuels containing alcohols, ethers, and ketones are being produced from the gases of the cracking process.

The increasing demand for motor fuel has led to ingenious methods of supplying the demand, depending upon whether a country has oil supplies or not.   Hydrogenation of coal, carbon monoxide, and heavy oils has made available enormous sources of motor fuel from the coal deposits of the world.   The motor fuel produced by the hydrogenation of coal has an octane rating of 72.   Motor fuel produced from carbon monoxide has an octane rating of 40; by the cracking process this fuel is converted into high-octane gasoline.   The hydrogenation of petroleum oils is carried out primarily for the purpose of producing solvents and lubricants.

Motor fuel is being produced by the distillation of oil shale, followed by cracking the hydrocarbons produced therefrom into gasoline of octane ratings from 60 to 75.   Countries having little or no crude oil sources are converting plants such as corn, wheat, barley, and potatoes into alcohol by the fermentation process.   The alcohol thus produced is used in part as motor fuel.   Wood is converted into a gaseous motor fuel which is used in busses and trucks, of which there are many hundreds in Italy, Germany, and France.   The wood is burned in equipment which is a part of the motor bus or truck in the engine of which the gas is burned.

The antiknock values of the motor fuels producible by the above meth-

ods and from the sources mentioned may be still further improved by solvent extraction of hydrocarbons and by the addition of tetraethyl lead.   The low-octane hydrocarbons extracted by solvents are readily converted into high-octane fuel by the cracking process.

By chemical and physical means it is possible to produce motor fuels of the desired octane rating in any volume required.

II. MOTOR FUEL FROM CRUDE OIL

A. General

During the past twenty years a tremendous amount of research work has been carried out on the art of distilling crude oil.   Distillation units with capacities ranging from a few hundred to over sixty-five thousand barrels of crude oil per day have been developed to fractionate the gasoline present with such nicety that almost no further refining is required.   The gasoline produced in the earlier days of distilling petroleum was treated with sulfuric acid and caustic soda and then redistilled to a commercial product. Today acid treatment is no longer necessary, for gasoline derived by distillation of crude requires, in general, no refinement beyond sweetening.

The antiknock value of straight-run gasoline varies widely, its octane number ranging from approximately 15 to over 70 (very little of the latter is available) and averaging about 53.   This average value is too low for modern high-compression engines and is in part reformed or cracked, i.e., the straight-chain paraffins which have low octane ratings are converted by heat and pressure into olefinic, aromatic, and naphthenic hydrocarbons which have greater antiknock properties

The cracking of hydrocarbon oils, such as gasoline, naphtha, kerosene, gas oil, fuel oil, or crude oil, produces gasolines the octane numbers of which range from approximately 60 to over 80, with an average of about 68. The quality of the cracked gasoline depends upon the type of oil processed and the time, temperature, pressure, and principle of operation used.

The volumes of straight-run and cracked gasolines produced from the various oil fields in the United States (73) for the year 1936 are shown in table 1.   For the first time in history, the production of cracked gasoline, representing 50.9 per cent of the total, surpassed that of straight-run gasoline.

B. Straight-run gasoline from distillation of crude oil

The distillation of crude oil at atmospheric pressure may be carried out in a unit (76, 17) such as shown in figures 1 and 2, using Pennsylvania crude as an illustration.   The crude oil, before passing through the heating coil of the furnace, is pumped through a series of heat exchangers counterflow to the hot vapors and liquids leaving the bubble tower fractionator.

The temperature of the oil is about 800°F. as it leaves the heating coil and flows into the fractionating column. The products derived from this primary distillation of Pennsylvania crude oil (42–43° A.P.I. gravity) are gasoline, naphtha, kerosene, furnace oil, fuel oil, wax distillate, and heavy lubricating oil stock and bottoms. The percentages and properties of these products are shown in tables 2 and 3.

Octane ratings and laboratory inspection data for a number of motor fuels derived from the distillation of crude oils, as produced in the Appalachian, Michigan, Indiana, Illinois, Kentucky, Mid-Continent, Gulf

TABLE 1

Volumes of straight-run and cracked gasoline produced in various sections of the United States (73) during 1936

REFINERY LOCATION*	CRUDE OIL		STRAIGHT-RUN GASOLINE		CRACKED GASOLINE	
	Thousand barrels	Per cent of total	Thousand barrels	Per cent of total	Thousand barrels	Per cent of total
1. Pennsylvania East Coast	27,072	2 5	39,145	16 9	52,610	22.0
2. Indiana, Illinois, Michigan, Kentucky, etc	25,074	2 3	35,252	15 3	46,794	19 5
3. Mid-Continent:						
Texas Inland	256,695	23 4	20,902	9 0	13,015	5.4
Oklahoma and Kansas	376,212	34 2	33,605	14 5	25,866	10.8
Arkansas and Louisiana Inland	37,364	3 4	5,554	2 4	4,320	1.8
4. Gulf Coast.	139,160	12 7	50,057	21.7	67,858	28 3
5 Rocky Mountain	22,166	2 0	5,811	2 5	5,113	2 1
6. California	214,773	19.5	40,961	17 7	24,044	10 1
Total . . .	1,098,516	100 0	231,287	100 0	239,620	100.0

* It should be noted that the figures for the production of gasoline are based on the location of the refinery rather than on the source of the crude.

Coast, Rocky Mountain, and California fields, are shown in table 4. With the exception of those obtained from White Castle, Louisiana, and Smackover, Arkansas (octane ratings 69 to 70), the straight-run gasolines have relatively low octane ratings; yields range from 2.0 per cent for the crude from Placedo, Texas, to over 81 per cent of a 400°F. end-point gasoline from a crude in Medicine Bow, Wyoming. Additional data on octane ratings and yields of the straight-run gasolines from different crude oils are given as follows: (*1*) Appalachian:—straight-run gasolines from Pennsylvania crude have octane ratings ranging from 35 to 50. (*2*) Michigan, Indiana, Illinois, and Kentucky:—Michigan straight-run

gasolines range in antiknock value from 17 to 43   (3) Mid-Continent:—
Texas straight-run gasolines have octane ratings between 55 and 61; the
amounts recovered from various crudes have ranged from 22 to 35 per
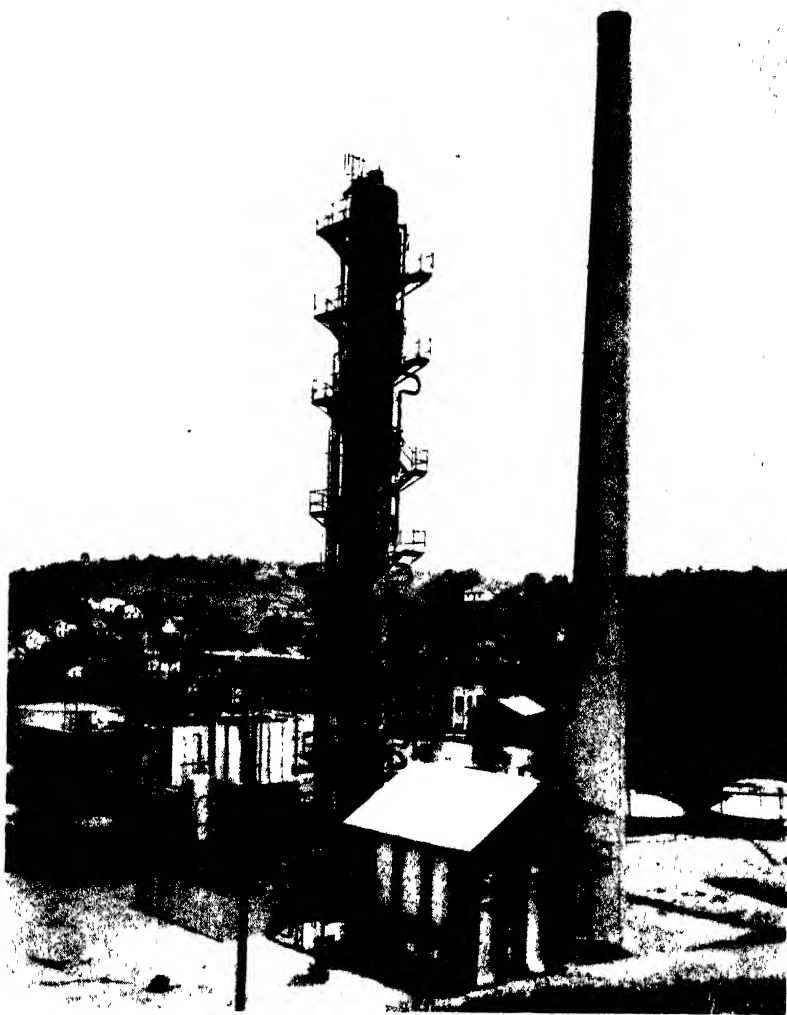
Fig 1 Crude-oil distillation unit in Pennsylvania

cent   (4) Gulf Coast:— crudes obtained from White Castle (Louisiana)
and Placedo (Texas) are typical of the general run of Gulf Coast crudes.
They usually contain small amounts of high-octane (of the order of 70

octane) straight-run gasoline   The newer fields in the Gulf Coast area, such as Flour Bluff (Texas) and La Fitti and Gilhs (Louisiana) yield straight-run gasolines of lower octane number, the range being from 45

	PRODUCTS PRODUCED OPERATING WITH VARIOUS CHARGING STOCKS		
	PRIMARY OPERATION	ALTERNATE OPERATION N°1	ALTERNATE OPERATION N°2
	PENNA GRADE CRUDE	BRIGHT STOCK SOLUTION	PRESSED DISTILLATE
66° A P I GASOLINE	66° A P I GASOLINE	SOLVENT NAPTHA	GAS OIL
51° A P I NAPTHA			
45.3° A P I KEROSENE			
41° A P I FURNACE OIL			
38° A P I FUEL OIL			NEUTRAL
33.3° A P I WAX DISTILLATE			NEUTRAL
28'/30° A P I SLOP WAX			NEUTRAL
LONG RESIDUUM 600 STOCK 650 STOCK		BRIGHT STOCK	180 VIS STOCK

FLEXIBILITY IN DISTILLATION UNIT

Fig. 2 Flow chart of crude-oil distillation unit

TABLE 2

Products derived from primary distillation of Pennsylvania 42-43° A P I gravity crude oil (76, 17)

PRODUCT	GRAVITY AT 60°F		MAKING 600 FIRE STOCK		MAKING 665 FIRE STOCK	
	°A P I	Specific	Barrels per day	Per cent	Barrels per day	Per cent
Gasoline*	66 0	0 717	633	25 3	625	25 0
Naphtha	51 1	0 775	242	9 7	250	10 0
Kerosene	45 7	0 799	362	14 5	375	15 0
Furnace oil	40 0	0 825	213	8 5	125	5 0
Fuel oil	38 0	0 835	100	4 0	175	7 0
Wax distillate	33 4	0 858	475	19 0	550	22 0
Bottoms†	25 0	0 904	475	19 0	400	16 0
Total			2500	100 0	2500	100 0

*The light gasoline shown, having an A P I gravity of 80 and representing 3 5 per cent of the crude or 13 8 per cent of the total gasoline, was preflashed and not fractionated This product is usually blended with the heavy gasoline to produce the 66° A P I gravity shown

†While the unit was designed for taking off a slop wax, the fraction usually is sufficiently sharp to eliminate the necessity of this cut

to 47. (5) Arkansas and Northern Louisiana:—The Smackover field is the largest producer in Arkansas. The crude is of low gravity and contains small amounts of high-octane straight-run gasoline. The Rodessa field in Northern Louisiana, the largest producer in that area, yields a low-octane straight-run gasoline. (6) Rocky Mountain:—This area produces all types of crudes, the most unusual being that from Medicine Bow (Wyoming) which has yielded 81 per cent of 400°F. end-point straight-run

TABLE 3

Properties of products from primary distillation of Pennsylvania 42-43° A.P.I. gravity crude oil (76, 17)

PROPERTIES	GASOLINE*		NAPH-THA	KERO-SENE	FUR-NACE OIL†	FUEL OIL†	BOT-TOMS, 665 FIRE STOCK‡
	Light	Heavy					
Gravity, °A.P.I	80 0	64 0	51.1	45 7	40 0	38.0	25.0
Distillation characteristics:							
Initial boiling point, °F	70	120	305	400	340	540	
10 per cent	100	175	330	413	491	583	
20 per cent	115	196	334	418	512	589	
50 per cent	158	237	344	433	528	601	
90 per cent	258	293	375	468	550	622	
End point, °F	270	320	419	498	574	635	
Flash point, °F				185			590
Fire point, °F				205			665
Flash point P.M., °F							590
Viscosity, S.U. at 210°F							202

* The light gasoline shown, having an A.P.I gravity of 80 and representing 3.5 per cent of the crude or 13.8 per cent of the total gasoline, was preflashed and not fractionated. This product is usually blended with the heavy gasoline to produce the 66° A.P.I. gravity gasoline shown in table 2.

† Furnace oil and fuel oil may be varied as the market demands.

‡ While the unit was designed for taking off a slop wax, the fraction usually is sufficiently sharp to eliminate the necessity of this cut.

gasoline having an octane rating of 58. The straight-run gasolines in the entire field range in octane number from 17 to 58. The gasoline having an octane number of 17 comes from Baker (Montana) crude oil. (7) California:—The octane numbers of straight-run gasolines from California crude oil generally range from 52 to 66. The lighter crude oils are produced in the Signal Hill district and the heavier crudes come from the Los Alamos and Santa Maria fields. The heavier crudes are usually higher in sulfur content.

TABLE 4

Octane ratings and inspection data for straight-run gasolines from various crude oils

CRUDE OIL-PRODUCING FIELDS AND DISTRICTS	APPALACHIAN	CALIFORNIA		GULF COAST			MICHIGAN, INDIANA, ILLINOIS	MID-CONTINENT			ARKANSAS AND NORTHERN LOUISIANA		ROCKY MOUNTAIN	
	Corning, Ohio	Signal Hill light crude	Los Alamos heavy crude	White Castle, Louisiana	Piscedo, Texas	Flour Bluff, Texas	Mt. Pleasant, Michigan	Kansas	East Texas	West Texas (Howard-Glasscock)	Smackover, Arkansas	Rodessa, Louisiana	Hot Lake, Wyoming	Pondera, Montana
Crude oil:														
Gravity, °A.P.I	35.0	25.2	14 1	24 0	24 4	43 2	40 7	38.9	39 9	29 5	20.5	42 7	34.9	31 6
Straight-run gasoline:														
Yield, per cent of crude	25.2	20 7	12.7	4 6	2 0	26 0	35 9	35 0	35 0	22 3	10 5	36 6	28.1	34 5
Gravity, °A.P.I	58 5	52 8	54 3	46 4	No analysis because of low gasoline content	59 9	62 5	60 5	64 3	55 0	47.3	59.6	59.9	58 9
Octane No., C.F.R. motor method	Approx 42	58	61	Approx. 70		46	22	45	55	61	69	33	58	43
Sulfur, per cent	0.03	0 10		0 02		0 02		0 03	0 02		0 06	0 04	0 01	
Distillation characteristics:														
Initial boiling point, °F	140	144	118	127		120	107	110	89	106	183	130	99	142
5 per cent	170	202	166	214		170	142	154	122	149	221	167	141	170
10 per cent	193	220	188	240		186	162	171	142	174	233	186	160	188
20 per cent	222	240	217	266		212	193	196	172	208	255	210	187	214
50 per cent	276	282	280	301		267	269	259	236	276	312	280	251	273
90 per cent	350	349	355	358		325	364	347	348	358	375	360	352	362
End point, °F	400	400	400	400		374	401	398	401	400	428	399	398	402
Per cent over	98.5	99.0	98.0	98 5		98 0	98 5	98 0	97 5	98 0	98 5	98 5	98 0	98 0
Per cent bottoms	1 0	1.0	1.0	1 0		1 0	1.0	1 0	1 0	1 0	1 5	1 0	1 0	1 0
Per cent loss	0 5	0 0	1.0	0 5		1 0	0 5	1 0	1 5	1 0	0 0	0 5	1 0	1.0

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C. Cracking

1. Straight-run gasolines and naphthas

In view of the increasing number of high-compression motors in use, straight-run gasoline is no longer suitable as a fuel. It is necessary to convert it into suitable hydrocarbons which possess greater antiknock properties. The branched-chain paraffins are the most desirable type at this time (September, 1937); however, olefins, naphthenes, and aromatics are suitable. To convert the knocking gasolines into non-knocking ones, they are subjected to temperatures of the order of 1025°F. and pressures of the order of 750 lb. It is estimated that 25 per cent of the 231,587,000 barrels of straight-run gasoline and naphtha produced during 1936 was reformed (cracked) into gasoline of higher octane numbers. The reforming of gasoline is increasing in order to meet the demand for high-octane gasoline.

Octane ratings and laboratory inspection data for reformed and cracked gasolines, as produced from various crudes, are given in tables 5 and 6.

As noted in table 5, the reforming stocks varied from straight-run naphtha to light gasoline   Yields of reformed gasoline with octane ratings of 57 to 80 ranged from 38 per cent to more than 88 per cent, depending upon the cracking plant operating conditions and the type of stock used.

2. Heavy oils to gasoline

The modern refining of crude oil, when only gasoline is the desired end-product, takes place in combination topping and cracking units. As noted in table 6, in some cases the whole crude was subjected to cracking conditions of heat and pressure to produce the cracked fuel. In other cases either the topped or reduced crude was utilized. The yields of cracked gasoline, based upon the charge, ranged from 44 per cent to over 63 per cent, with ratings from 68 to 77 octane number. It should be mentioned, however, that both the yield and the quality of the gasoline produced are dependent upon the cracking stock and upon such operating conditions as time, temperature, and pressure.

A flow chart of a topping and cracking unit handling 12,500 barrels of California crude oil per day is shown in figure 3. The cracking section is based upon the selective principle, which uses two or more heating coils in order that each fraction of the oil may be converted under its best time, temperature, and pressure conditions.

The crude oil charged to the unit usually contains water as an emulsion, together with dissolved salts, which it is desirable to remove before processing in the unit. To accomplish this, the crude oil is pumped through a heat exchanger under a pressure of approximately 165 lb. per square inch,

TABLE 5

Octane ratings and inspection data for reformed straight-run gasolines and naphtha from various crude oils

CRUDE OIL-PRODUCING FIELDS AND DISTRICTS	Appalachian-Pennsylvania Light gasoline	Appalachian-Pennsylvania Gasoline	Appalachian-Pennsylvania Naphtha	Mt Pleasant, Michigan Gasoline	Mid-Continent Gasoline	Mid-Continent Naphtha	East-West Texas Gasoline (1)	(2)	(3)	(4)	(5)	(6)	West Texas Gasoline	West Texas Naphtha	Rocky Mountain-Montana Gasoline	California Light naphtha	California Heavy naphtha
Type of reforming stock																	
Charging stock:																	
Gravity, °A.P.I	64.4	58.1	49.8	61.7	59.8	53.6	58.8	Same	Same	Same	Same	Same	58.1	51.5	59.8	46.6	42.4
Sulfur, per cent				0.04			0.14	Same	Same	Same	Same	Same	0.18	0.19	0.11	0.10	0.09
Octane No., C.F.R. motor method	49	38	27	20	42	34	54	Same	Same	Same	Same	Same	60	50	51	50	48
Distillation characteristics:																	
Initial boiling point, °F	117	152	272	152	115	222	99	Same	Same	Same	Same	Same	95	220	126	303	299
10 per cent	169	215	315	190	177	263	168	Same	Same	Same	Same	Same	160	261	186	311	325
50 per cent	192	280	329	278	277	309	262	Same	Same	Same	Same	Same	374	312	212	320	361
90 per cent	301	354	446	360	347	353	360	Same	Same	Same	Same	Same	364	370	340	340	400
End point, °F	354	390	479	389	383	385	406	Same	Same	Same	Same	Same	392	410	381	364	427
Operating conditions:																	
Pressure, lb. per square inch	750	500	478	1000	500	500	750	752	750	750	745	750	750	750	500	750	750
Furnace discharge, °F	975	975	975	985	1000	1000	945	966	975	994	995		950	950	965	975	970
Reaction chamber, °F	925	926	924	935	950	952	899	909	925	943	993	995	898	899	915	925	922
Feed rate, gallons per hour	1.97	0.76	1.04	1.98	1.91	2.03	2.01	1.94	1.98	3.93	3.02	2.06	3.20	2.13	1.95	1.37	2.02
Cracking results:																	
Gasoline:																	
Yield, per cent of charge	72.2	66.5	64.0	65.5	74.7	74.3	88.7	82.7	76.0	62.8	46.9	37.9	88.1	81.1	79.5	69.2	70.5
Gravity, °A.P.I	63.5	57.3	54.5	61.0	59.1	55.5	58.8	58.7	58.2	52.2	49.2	45.7	59.4	54.5	60.7	48.3	47.5
Octane No., C.F.R. motor method	70	74	74	67	70	70	68	71	72	76	78	80	72	73	72	77	77
Distillation characteristics:																	
Initial boiling point, °F	99	84	88	94	89	91	101	96	96	102	100	106	96	91	96	93	88
10 per cent	148	154	145	142	146	164	150	146	154	186	158		148	171	146	179	178
20 per cent	172	188	192	193	180	204	176	174	186	254	184		178	214	176	236	236
50 per cent	229	252	289	235	259	280	245	242	236	254	244	234	253	280	243	296	316
90 per cent	320	384	397	360	356	358	364	372	354	397	362	359	366	378	336	350	380
End point, °F	363	404	410	396	379	382	403	411	396	435	416	429	400	403	386	381	400
Residuum:																	
Yield, per cent of charge	2.5	4.6	7.6	4.3	1.3	2.5	0.0	0.6	3.5	1.1	5.3	5.7	2.1	5.7	3.8	8.2	12.8
Gravity, °A.P.I	15.0	2.9	17.2	8.5	-0.7	-4.5		20.8	16.1	7.1	2.8	0.3	12.9	11.7	14.6	9.1	17.7
Gasoline content, per cent	3.5	0.0	0.0	0.5				5.0	2.0	3.0	1.8	2.0	3.5	4.0	3.0	3.0	2.0
Loss:																	
Liquid volume, per cent	25.3	28.9	28.4	30.2	24.0	23.2	11.3	16.7	20.5	36.5	45.8	56.4	9.8	13.2	16.7	22.6	16.7
Gas, cu. ft. per barrel of charge	645	946	919	789	611	762	380	499	640	1125	1430	1780	369	535	778	695	735

TABLE 6

Octane ratings and inspection data for cracked gasolines from various crude oils

CRUDE OIL-PRODUCING FIELDS AND DISTRICTS.	APPALACHIAN	MICHIGAN, INDIANA, ILLINOIS	MID-CONTINENT					GULF COAST			ROCKY MOUNTAIN		CALIFORNIA	
	Corning, Ohio	Mt. Pleasant, Michigan	Kansas	East Texas	West Texas	Smackover, Arkansas	Rodessa, Louisiana	White Castle, Louisiana	Placedo, Texas	Flour Bluff, Texas	Rex Lake, Wyoming	Pondera, Montana	Signal Hill	Los Alamos
Type of cracking stock	Reduced crude	Topped crude	Topped crude	Reduced crude	Heavy naphtha and topped crude	Topped crude	Topped crude	Whole crude	Whole crude	Reduced crude	Topped crude	Topped crude	Topped crude	Whole crude
Cracking stock:														
Yield, per cent of crude	68.0	65.7		52.9	90 0	89.8	63.2	100	100	24.1	70.4	61.9	83.2	100
Gravity, °A.P.I	28.4	31.0	25.5	26.6	27 4	17.9	35.0	24.0	24.4	27.8	27.4	20.1	20 6	14.1
Cracked gasoline:														
Yield, per cent of cracking stock	61.0	63.5	57.9	54.5	61.0	43.7	61.7	59.0	58.6	57 4	59.8	51.4	48 2	44.1
Gravity, °A.P.I	59.4	62.3	60.4	59.9	56.0	57.5	63.7	52.7	51.3	59.5	59.0	58.9	56.9	54.0
Octane No., C.F.R. motor method	Approx. 68	64	71	68	69	72	70	Approx. 80	77	70	70	68	71	72
Sulfur, per cent	0.08	0.05	0 06	0.07	0.23	0.26	0.05	0 06	0.06	0.03	0.09	0 29	0.55	1.84
Distillation characteristics:														
Initial boiling point, °F	90	92	88	90	99	91	96	104	95	97	96	90	99	98
5 per cent	126	125	124	112	132	126	116	132	134	122	123	123	127	133
10 per cent	146	143	136	124	157	140	130	153	154	137	138	144	145	155
20 per cent	182	172	164	156	198		157	190	192		162	180	177	193
50 per cent	268	246	236	244	284	262	226	280	277	243	256	270	304	270
90 per cent	390	342	346	364	384	364	334	376	372	342	355	370	357	306
End point, °F	404	374	406	404	394	397	393	399	401	412	395	397	396	400
Per cent over	98.0	98.0	98.0	97.0	97.0	97.5	97.5	97 0	95.0	98.0	97.0	95.0	98.0	94.5
Per cent bottoms	1.0	1.0	1.0	1.0	1.5	1.0	1.0	1.5	1.0	1.0	1.0	1.0	1.0	1.0
Per cent loss	1.0	1.0	1.0	2.0	1.5	1.5	1.5	1.5	4.0	1.0	2.0	4.0	1.0	2.5
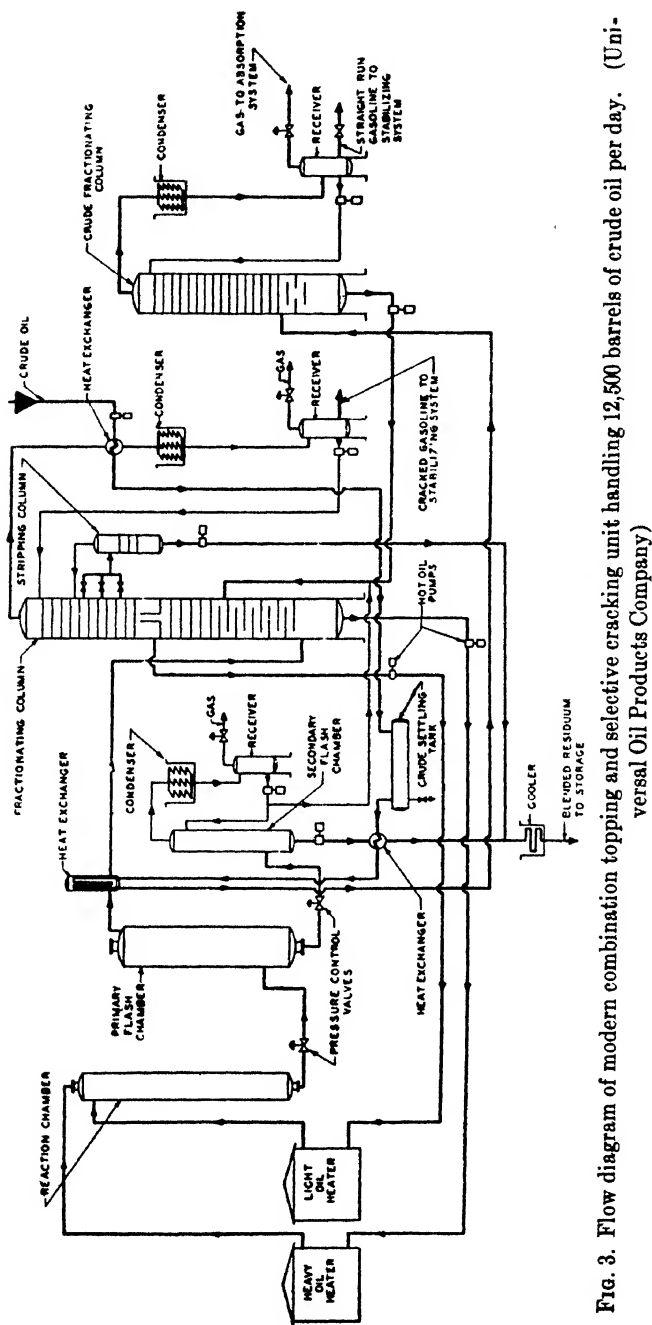
Fig. 3. Flow diagram of modern combination topping and selective cracking unit handling 12,500 barrels of crude oil per day. (Universal Oil Products Company)

where the temperature of the oil is raised to 225°F. It is then passed to a settling chamber Under these conditions of temperature and pressure the viscosity of the crude oil is reduced, but vaporization of the water is prevented As a result, the salt water drops out and is removed from the bottom of the settler

The crude oil then flows from the top of the settling tank through a series of heat exchangers to increase the temperature to approximately 550°F The preheated oil is passed to the crude oil-fractionating column,
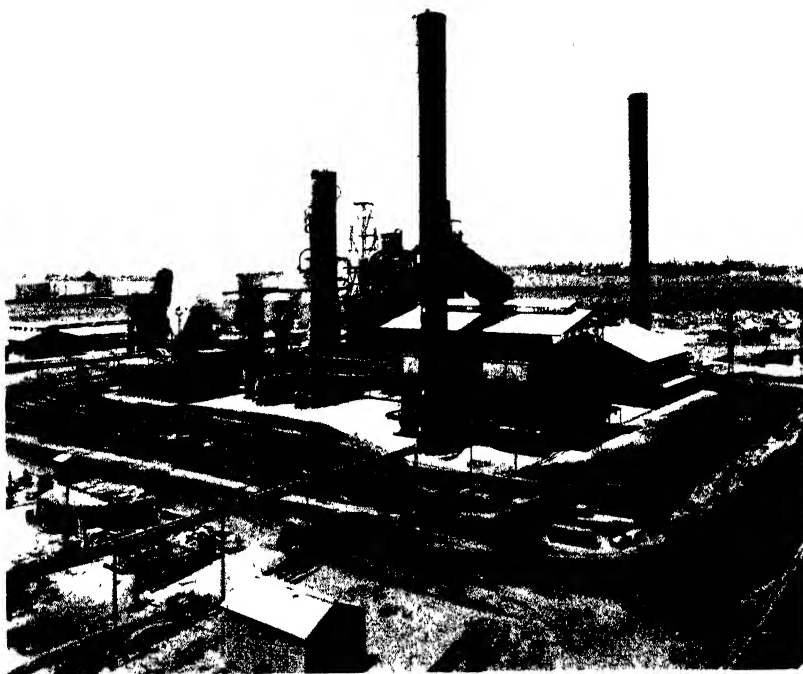
Fig 4 Topping and cracking unit handling 15,000 barrels per day

where the gasoline is distilled and then condensed, flowing to a storage tank. The fractionating column for this service is 11 ft in diameter and 49 ft high The topped crude from the bottom of the fractionating column is pumped directly to the bubble tower of the cracking unit The cracking unit fractionating column is 11 ft in diameter and 74.5 ft high. The topped crude passing down through this column contacts the hot ascending vapors and a partial fractionation takes place. The vapors passing up the column are separated as a liquid sidecut and an overhead consisting of gasoline and gas The liquid sidecut, called light oil, is pumped from one

of the bubble decks to the light-oil furnace tubes and heated to a temperature of approximately 960°F   The gasoline vapors and gas pass from the top of the fractionating column through a cooling coil to a receiver, where a separation of gasoline and gas is made   The unconverted oil from the bottom of the fractionating column, referred to as heavy combined feed and consisting of the heavy ends of both the charge and the vapors condensed in the tower, is pumped through the heavy-oil furnace tubes, where the temperature is raised to approximately 925°F

The ratings of the light- and heavy-oil heaters are 53 and 61 million B t u per hour absorbed by the oil   The outlet pressures of the two heaters are 300 and 280 lb per square inch, respectively   The heated hydrocarbons from both these heaters pass to the top of the reaction chamber, which is 7 ft in diameter and 50 ft high and is maintained at a pressure of 275 lb

The hydrocarbon mixture from the bottom of the reaction chamber passes to the primary flash chamber, which is 11 ft in diameter and 40 ft high   The flash chamber and subsequent equipment through the condenser to the receiver are maintained at a pressure of approximately 100 lb   The material entering the flash chamber is separated into bottoms of cracked unflashed residue and overhead vapors of gas, gasoline, and recycle stock   The vapors from the top of the flash chamber pass through a heat exchanger into the fractionating column, where they contact the topped crude oil as previously described   The unflashed residue passes to a secondary flash chamber, which is 6 ft in diameter and 28 5 ft high, maintained at about 20 lb pressure   The material entering this chamber separates into low-gravity cracked residuum bottoms and overhead vapors which are returned to the fractionating column   The residuum is blended with part of the sidecut of the column to produce a blended residue meeting fuel-oil specifications.

The vapors from the top of the fractionating column, at a temperature of 380°F , pass through heat exchangers and a condenser into a receiver, where a separation of the gas and cracked gasoline is made   The cracked gasoline has the required end point and flows to a stabilizer to produce the required vapor pressure, which normally varies from 8 to 12 lb. (Reid at 100°F) depending upon the season of the year   The cracked gasoline may be water-washed, caustic soda-treated, or sweetened and then fortified against deterioration by antioxidants   It may be colored by a dye, and as such is suitable for marketing

A typical commercial run of thirty days in the described plant, processing 373,650 barrels of California crude oil at the rate of 12,500 barrels per day, produced an average of 64 03 per cent motor fuel, 28.86 per cent 5 1° A P I gravity cracked fuel oil, and 7 11 per cent gas and loss   A sum-

mary of the operating conditions used and of the volumes and properties of the products produced is given in tables 7 and 8.

TABLE 7

Summary of operatıng conditions used and volumes of products produced when topping and cracking California crude oil

OPERATION AND PRODUCTS	TOTAL NUMBER OF BARRELS	BARRELS PER DAY	PER CENT OF CHARGE
Topping operation:			
Crude oil . . .	373,650	12,455	100 00
Products:			
Straight-run gasoline	119,670	3,989	32.03
Topped crude . .	250,200	8,340	66.96
Gas and loss . .	3,780	126	1.01
Totals . .	373,650	12,455	100.00
Cracking operation:			
Topped crude. .	250,200	8,340	100 00
Products:			
Cracked gasoline	119,580	3,986	47.79
Cracked residuum	107,820	3,594	43 09
Gas and loss	22,800	760	9.12
Totals . . .	250,200	8,340	100 00
Combination topping and cracking operation:			
Products processed:			
Crude oil . .	373,650	12,455	100.00
Products:			
Straight-run gasoline	119,670	3,989	32.03
Cracked gasoline	119,580	3,986	32.00
Total gasoline	239,250	7,975	64.03
Cracked residuum	107,820	3,594	28.86
Gas and loss . .	26,580	886	7.11
Totals... .	373,650	12,455	100.00

Time on stream = 30 days; total gas produced = 122,400,000 cu. ft.

D. Commercial gasolines and their properties

The average octane ratings and volatility of commercial gasolines as marketed in certain parts of the United States during the last ten years (80) are shown in table 9. It is interesting to note the trend toward higher volatility and increased octane ratings during this period: for the premium grade, an increase of 5 octane numbers resulted during the past six years; for the regular grade, an increase of 10 octane numbers; and for

the third grade (largely straight-run gasoline), an increase of 3 octane numbers.

Studies of the properties of motor fuels conducted by the U. S. Bureau of Mines and the Coöperative Fuel Research Committee (74) for the winters of 1935–36 and 1936–37 indicate somewhat higher octane ratings for regular- and premium-price gasolines and somewhat lower for third-grade products during the winter of 1936–37. The average results for eighteen marketing areas in the United States are shown in table 10. Other properties of the three grades of motor fuels are shown in tables 11, 12, and 13.

TABLE 8

Laboratory analyses of straight-run and cracked gasoline produced when topping and cracking California crude oil

PROPERTIES	CRUDE OIL	STRAIGHT-RUN GASOLINE	CRACKED GASOLINE	BLENDED RESIDUE
Gravity, °A.P I	30 5	52 1	59 6	5.1
Distillation characteristics:				
Initial boiling point, °F	156	126	102	
10 per cent	277	199	142	
30 per cent	441	248	184	
50 per cent	583	287	241	
90 per cent	687	389	344	
End point, °F		425	383	
Per cent distilled at 300°F	12			
Per cent distilled at 400°F	26			
Octane No., C.F.R. motor method		56	71	
Reid vapor pressure, lb. per square inch at 100°F		5 0	9 3	
Sulfur, per cent	0.65	0 06	0 37	
Color		25		
Viscosity, S F. at 122°F				240
Flash point, P.M., °F				194
B. S. & W., per cent				0.1

E. Tractor fuels

Distillates, kerosene, and gasoline are used as tractor fuels. In many cases such fuels are raw or unfinished products. Although a number of tractors are operated on gasoline, the majority still burn kerosene or distillates such as furnace oils, with kerosene gradually being replaced by the lower-grade distillate fuels.

As for the use of gasoline as tractor fuel, it is claimed that consumer demand for high-compression gasoline-burning tractors is increasing at a rapid rate (53). Such engines are now available either as standard or

TABLE 9

Volatility and octane ratings of average commercial gasolines (80)

GASOLINE AND PROPERTIES	YEAR										
	1927	1928	1929	1930	1931	1932	1933	1934	1935	1936	1937
Premium grade:											
Octane No., C.F.R. motor method						72	74	76	75	75	76	77
Distillation characteristics:											
Initial boiling point, °F.	117	106	106	94	94	97	96	93	94	91	93
10 per cent	161	153	157	140	141	146	142	136	132	129	126
20 per cent	191	187	185	174	170	171	177	163	157	153	150
50 per cent	257	253	257	256	246	243	237	235	225	223	219
90 per cent	371	370	362	365	361	352	350	344	338	338	332
End point, °F	421	419	404	407	403	363	399	394	392	392	386
Recovery, per cent	98.0	97 7	98.0	97.0	97 6	96 9	96.4	97.1	96 9	96.4	96.5
Reid vapor pressure, lb per square inch at 100°F					7.5	8.1	9.0	8.8	9.6	10.2	9.2
Regular grade:											
Octane No., C.F.R. motor method						60	61	65	69	69	69	70
Distillation characteristics:											
Initial boiling point, °F	114	99	104	97	97	94	94	92	90	87	89
10 per cent	160	146	150	149	148	143	139	135	127	127	125
20 per cent	192	180	185	182	182	173	166	163	153	155	150
50 per cent	269	267	271	261	255	256	247	242	231	236	240
90 per cent	375	379	381	375	373	377	365	354	352	359	358
End point, °F	426	426	423	416	411	404	406	403	400	406	401
Recovery, per cent .	97 8	97.4	97 8	96.5	96.9	96 7	96.5	96 7	96 4	96.2	96.2
Reid vapor pressure, lb. per square inch at 100°F					6 4	9.0	9.5	9 5	10.4	11.1	10.3
Third grade:											
Octane No., C F.R. motor method ..						51	53	53	52	51	54
Distillation characteristics:											
Initial boiling point, °F	94	94	95	87		102	96	94	97	99	97
10 per cent . ..	130	146	137	143		152	148	146	148	154	143
20 per cent . ..	162	180	170	177		193	181	180	181	185	173
50 per cent . . .	300	264	265	267		276	264	252	261	257	248
90 per cent	436	386	391	404		380	368	367	373	371	361
End point, °F	456	422	429	437		426	426	425	421	416	411
Recovery, per cent ..	96 0	96.0	96.5	95.5		97.3	97.3	97.5	97 0	96.7	96.7
Reid vapor pressure, lb. per square inch at 100°F ..						6.5	7.6	8.4	7.8	8.0	8.0

TABLE 10

*Comparative octane ratings for regular-, premium-, and third-grade gasolines (74)
for the winters of 1935-36 and 1936-37*

FUEL	OCTANE NO.	
	Winter 1935-36	Winter 1936-37
Regular grade:		
Minimum rating	61	64
Maximum rating	72	68.9-71.4
Range of 90 per cent	68-71	74
Premium grade:		
Minimum rating	69.1	74
Maximum rating	81	83
Range of 90 per cent	73.7-80.5	75 4-80.7
Third grade:		
Minimum rating	33.5	44 8
Maximum rating	69 1	69 0
Range of 90 per cent	50-66	50 4-64 0

TABLE 11

Regular-price gasolines (74) for the winters of 1935-36 and 1936-37

PROPERTIES	WINTER OF 1935-36			WINTER OF 1936-37		
	Minimum	Range of 90 per cent	Maximum	Minimum	Range of 90 per cent	Maximum
Gravity at 60°F.:						
Specific	0 763	0 747-0.715	0.707	0 783	0 746-0.717	0.709
°A.P.I ..	54.0	58 0-66.5	68 6	49.2	58.3-65 9	68.2
Sulfur, per cent	0 014	0 02-0 15	0.30	0.007	0.028-0.14	0 35
Reid vapor pressure, lb. per square inch at 100°F	5.8	7.1-12.4	13.15	7.3	8.4-12.4	12.8
Copper strip test..		Negative			Negative	
Octane No., C.F.R. motor method	61	68-71	72	64	68.9-71.4	74
Distillation characteristics:						
Initial boiling point, °F	79	82-98	100	67	83-94	107
10 per cent.	108	114-144	155	107	115-144	160
20 per cent.	124	132-175	186	130	136-174	192
50 per cent	178	207-255	266	192	235-256	273
90 per cent	245	335-377	388	287	335-370	390
End point, °F	332	385-415	464	342	382-415	443
Per cent loss	0.9	1.0-3.5	5.0	0.8	1.0-3.4	5.0

TABLE 12

Premium-price gasolines (74) for the winters of 1935-36 and 1936-37

PROPERTIES	WINTER OF 1935-36			WINTER OF 1936-37		
	Mini-mum	Range of 90 per cent	Maxi-mum	Mini-mum	Range of 90 per cent	Maxi-mum
Gravity at 60°F.:						
Specific.	0.779	0.749-0.702	0.684	0.783	0.747-0.710	0.676
°A.P.I .	50 1	57.5-70 0	75 4	49.3	57.9-67 9	77.7
Sulfur, per cent .	0.006	0.02-0.08	0.179	0.007	0.022-0.19	0 165
Reid vapor pressure, lb. per square inch at 100°F	3.1	5.0-11 5	12.55	5.5	7.3-11.2	12.2
Copper strip test		Negative			Negative	
Octane No., C.F.R. motor method	69 1	73.7-80.5	81	74	75.4-80 7	83
Distillation characteristics:						
Initial boiling point, °F	76	84-107	128	80	86-103	116
10 per cent	110	115-150	178	110	117-150	158
20 per cent .	117	134-176	201	117	134-175	187
50 per cent	143	180-252	261	136	185-250	259
90 per cent .	264	273-359	378	245	289-364	390
End point, °F	331	343-415	439	335	358-415	426
Per cent loss	0 5	1 0-3 0	3.6	0	0 9-2 8	4 0

TABLE 13

Third-grade gasolines (74) for the winters of 1935-36 and 1936-37

PROPERTIES	WINTER OF 1935-36			WINTER OF 1936-37		
	Mini-mum	Range of 90 per cent	Maxi-mum	Mini-mum	Range of 90 per cent	Maxi-mum
Gravity of 60°F.:						
Specific. . . .	0.757	0.753-0 724	0.704	0.759	0.751-0.729	0.717
°A.P.I . .	55.4	56.5-64 0	69 5	55	56.9-62 5	65.8
Sulfur, per cent. . .	0 016	0.02-0.20	0 23	0.005	0.021-0.13	0.27
Reid vapor pressure, lb. per square inch at 100°F	4.2	5.5-10.4	13.4	2.6	5 7-9 8	10.7
Copper strip test. .		Negative			Negative	
Octane No., C.F.R. motor method . . .	33.5	50-66	69.1	44.8	50.4-64.0	69.0
Distillation characteristics:						
Initial boiling point, °F. . . .	78	84-104	128	76	86-104	143
10 per cent .	113	127-161	179	119	127-159	198
20 per cent.	128	150-196	205	141	160-195	219
50 per cent . .	184	230-276	282	216	229-278	283
90 per cent . .	292	330-393	399	312	335-386	391
End point, °F . . .	341	388-430	511	368	388-427	437
Per cent loss . . .	0.5	1.0-3.5	5.5	0	1.0-2.9	5.0

optional equipment on many makes of tractors. It is reported (53) that a tractor designed to operate on 70-octane gasoline will do approximately $33\frac{1}{3}$ per cent more work than a similar tractor with low compression using kerosene or a distillate fuel.

No specifications for tractor fuels as such have been issued by the A.S.T.M. Whatever specifications for this product may exist are chiefly

TABLE 14

Specifications adopted by the Western Petroleum Refiners Association for tractor fuels (78)

Flash point, °F , minimum .	110
Distillation characteristics, °F.:	
10 per cent, minimum	347
25 per cent, minimum	392
95 per cent, minimum	464
Color	−16 or darker

TABLE 15

Tractor-fuel specifications (78) of the State of Illinois

Flash point, 'F., minimum	100
Distillation characteristics, °F.:	
Initial boiling point, minimum	300
25 per cent, maximum .	392
90 per cent, maximum . .	450

TABLE 16

Tractor-fuel specifications (6) of the State of Minnesota

Distillation characteristics, °F :	
Initial boiling point, minimum	225
10 per cent, minimum	276
10 per cent, maximum .	347
90 per cent, minimum	464
End point, maximum	500
Color	−16 or darker

those prepared for marketing purposes and by state regulations. For example, the Western Petroleum Refiners Association has adopted the tractor-fuel specifications shown in table 14 to be used as a standard for members of the association (78). The regulations of the State of Illinois (78) are given in table 15.

A bill introduced recently into the Minnesota House of Representatives (6) calls for the specifications shown in table 16. Although the specifica-

tions given do not include octane rating, it has been suggested (78) that the octane numbers of tractor fuels should be above 30.

Octane ratings and laboratory inspection data on typical Mid-Continent straight-run and cracked fuels (78) are given in table 17.

F. Diesel fuels

Diesel fuels may be derived from petroleum, shale, coal tar, or vegetable oils. For high-speed engines it is generally agreed that fuels of a paraffinic nature give the best results; aromatic fuels are the least suitable. Between these two extremes lie fuels of the naphthenic and olefinic type, which

TABLE 17

Typical Mid-Continent straight-run and cracked products (78)

PROPERTIES	STRAIGHT-RUN PRODUCTS		CRACKED FURNACE OIL	
	Kerosene	Gas oil	No. 1	No. 2
Gravity at 60°F.:				
°A.P.I	42	32	37	28
Specific	0.82	0 87	0.84	0.89
Distillation characteristics:				
Initial boiling point, °F	350	370	325	375
10 per cent	390	430	380	430
90 per cent	470	640	440	635
End point, °F	510	700	490	700
Per cent at 392°F	10	2	15	
Flash point, °F	140	140	120	160
Octane No., C.F.R. motor method	0–10	Below 0	40–50	0–20
Heat content (net):				
B.t.u. per pound	18,600	18,200	18,600	18,300
B.t.u. pound per gallon	126,000	131,500	130,000	135,000

are suitable for the medium-speed and low-speed engines where fuel quality is of less importance.

Coal-tar oils, coal dust, and mixtures of coal and oil have been used as Diesel fuels, particularly in Germany (44, 43). They were found to be inferior to petroleum oils.

Vegetable oils such as peanut, cocoanut, soybean, and palm oils have also been used as Diesel fuels. Tests conducted with such fuels resulted in starting difficulties, low power output, and high fuel consumption (44, 43). In the natural state they contain gum-forming materials, but it is reported that they may be cracked to produce usable Diesel fuels.

Shale oils of Diesel boiling range may be mixtures of paraffinic, aromatic, naphthenic, or olefinic hydrocarbons. The shale oils of the paraffinic type have been found to be satisfactory for high-speed Diesel engines (44, 43).

The retorting of oil shale to produce oil, gas, and coke is in commercial operation in a number of foreign countries,—Scotland, France, Spain, Esthonia, Australia, and Manchuria. Oil production from shale is relatively expensive, and, despite a vast amount of research in the United States, to date no process has been found to allow it to compete successfully with petroleum.

It is apparent, therefore, that substantially all Diesel fuel for many years to come (at least in the United States) will be obtained from petroleum chiefly as straight-run and cracked distillates or mixtures thereof.

Distillate fuels are intermediate between gasoline and residual fuel oil. The maximum yield of straight-run distillate fuels would result only when none of the kerosene, gas-oil, and fuel-oil fractions of the crude oil was used

TABLE 18

Average yield of the various products produced from crude petroleum in the United States (73) for the year 1936

PRODUCTS OBTAINED FROM CRUDE PETROLEUM	THOUSAND BARRELS	PER CENT OF CRUDE
Crude petroleum	1,098,516	100 0
Motor fuels .	470,907	42 9
Straight-run	231,287	21 1
Cracked. . . .	239,620	21 8
Kerosene .	56,082	5 1
Gas oil and fuel oil .	411,338	37 4
Gas oil and distillates .	125,650	11 4
Fuel oil . .	285,688	26 .0
Still gas . .	54,441	5 0
Lubricants .	30,855	2 8
Other products and loss .	74,893	6 8

as cracking stock, and when all residual fuel was distilled to heavy tars or coke. On the other hand, the available supply of straight-run distillate fuels would be reduced either through an increased demand for cracking stock or through an increased demand for burner and heating fuels. The maximum available yield, if none was used for cracking and if all crude-oil distillation were carried to completion, might be as high as 65 to 70 per cent.

The proportion in which cracked and straight-run distillates are available from average crude by present refinery practice is shown in table 18. From each barrel of crude petroleum processed in 1936, a total of 42.5 per cent of kerosene, gas oil, distillate fuels, and fuel oil was produced (73). Although this total would not have been suitable for the high-speed Diesel, it is reasonable to believe that a percentage of the kerosene and

fuel-oil fractions could have been combined with the gas oil and distillate fuels to make available approximately 150 million barrels of suitable high-speed Diesel fuel. Most of the fuel-oil fraction would then be available for use in low-speed engines where fuel quality is of relatively less importance.

The quality of the straight-run and cracked Diesel fuels obtained from the various crude sources in the United States is indicated in table 19. It is apparent from a comparison of the data presented in table 19 and in table 20 that the straight-run fuels from each oil field are suitable for use

TABLE 19

Probable cetane ratings of straight-run and cracked Diesel fuels produced from various crudes in the United States

SOURCE OF CRUDE	1936 PRODUCTION (73)		PROBABLE AVERAGE CETANE RATINGS BY DELAY METHOD (44)	
	Thousand barrels	Per cent of total	Straight-run	Cracked
1. Appalachian:				
Pennsylvania	27,072	2.5	62	29
Kentucky and others	7,245	0 7	52	35
2 Michigan, Lima (Ohio), and North-eastern Indiana	12,586	1.1	68	37
3 Illinois and Southwestern Indiana	5,243	0.5		
4 Mid-Continent:				
East Texas	168,046	15 3	55	40
West Texas and Southeastern New Mexico	88,649	8.1	45	30
Oklahoma, Kansas, and Northern Texas .	376,212	34.2	56	35
Arkansas and Northern Louisiana	37,364	3.4		
5. Gulf Coast	139,160	12.7	58	41
6. Rocky Mountain .	22,166	2 0	51	38
7. California .	214,773	19.5	47	32
Total .	1,098,516	100 0		
Average cetane rating based on possible production			54	35

in the high-speed engine (with the possible exception of the aircraft Diesel). In many cases a considerable amount of cracked fuel may be blended with the straight-run fuel and the mixture will still meet the requirements of the high-speed and medium-speed engines.

The method each refiner uses to produce the required grades of Diesel fuel will depend upon the economics involved. In most cases it is believed that cracked distillates will constitute the base fuel, with straight-run products added in sufficient quantity to produce the proper ignition

manufacturers' recommended fuel specifications and A.S.T.M. Diesel fuel-oil classification for high-, medium-, and low-speed Diesel engines (48)

PROPERTIES	HIGH-SPEED (ABOVE 1000 R.P.M.) Twenty-five manufacturers		A.S.T.M. No. 1-D	MEDIUM-SPEED (500-1000 R.P.M.) Twenty-six manufacturers		A.S.T.M. No 3-D	LOW-SPEED (BELOW 500 R.P.M.) Thirty-three manufacturers		A.S.T.M. No. 4-D
	Spread	Average		Spread	Average		Spread	Average	
Viscosity, S.U. at 100°F.:									
(a) Seconds, minimum	34-40	36	35	34-75	40	35	30-75	40	
(b) Seconds, maximum	40-250	78	50	45-250	87	70	50-250	106	250
Gravity, °A.P.I:									
(a) Minimum	16-30	26		16-31	25		13-30	24	
(b) Maximum	29-45	35		29-45	36		19-45	34	
Sulfur, per cent, maximum	0-2 0	0.9	1 5	0-2 0	1 0	1.5	0-2 0	1 1	2.0
Hard asphalt, per cent, maximum	0.05-1 0	0 51		0 05-1 0	0.62		0 3-0 7	0.43	
Conradson carbon, per cent, maximum	0-3 0	0 6	0.2	0-5 0	1 0	0 5	0-10.0	1.7	3.0
Ash, per cent, maximum	0.01-0.05	0 03	0.02	0-0 1	0.04	0.02	0-0.15	0.04	0.04
Water and sediment, per cent, maximum	0-2 0	0.4	0.05	0-2 0	0.6	0.1	0-4.0	0 8	0.6
Flash point, °F., minimum	135-150	148	Legal	140-195	152	150	140-190	151	150
Pour point, °F., maximum		†	35‡		†	35‡		†	35‡
Distillation characteristics, °F.:									
(a) 10 per cent point maximum	460-475	465		460-510	485		660-750	705	
(b) 90 per cent point maximum	660-700	700		660-750	695		700	700	
(c) End point, maximum	650-700	680							
Ignition quality:*									
(a) Cetene No., C.C.R., minimum	38-45	42	45	40-50	45	35	35-50	43	
(b) Cetane No., C.C.R., minimum	45	45	45	45	45	30			
(c) Cetane No., delay, minimum	35-45	37		35-45	40		30-45	37	30
(d) Diesel Index No., minimum	35-40	38		40-50	45		40	40	20
(e) Viscosity-Gravity No., maximum			0.86			0 89			0.91
(f) Boiling point-Gravity No., maximum.			188			195			200

* Ignition quality values cannot be considered entirely representative because of the differences in nomenclature used for expressing same.

† 10-15°F. below operating temperature.

‡ Lower pour points may be specified whenever required by local temperature conditions.

quality characteristics.   The amount of each will depend upon the cetane ratings of both the straight-run and the cracked materials.

In the production of aircraft Diesel fuels where high ignition quality and low cloud and pour points are required, indications are that other than normal refining methods will be necessary.   Refined straight-run fuels of high ignition quality usually have high cloud and pour points, whereas cracked fuels of low ignition quality have low cloud and pour points.   It is apparent, therefore, that special methods of refining or treating will be necessary in the production of suitable aircraft fuels or fuels for other purposes where high ignition quality and low pour point are essential.   A number of these are as follows: (1) hydrogenation; (2) polymerization; (3) mild cracking; (4) dewaxing; (5) pour-point depressors; (6) acid treating; (7) solvent treating; and (8) Diesel dopes.

It is reported that hydrogenation produces fuels of high ignition quality and low pour point from either cracked or straight-run petroleum oils. With the proper selection of charging stock, indications are that fuels of 60 to 64 cetane number with pour points as low as $-40°$ to $-50°F$. may be prepared by this method.[1]

The hydrogenation process may be used also in the production of Diesel oils from coal.   A number of coal hydrogenation plants are now in operation in Europe.   At present, the principal product of these plants is gasoline, although efforts are being made toward the production of suitable Diesel fuels.   In one installation (20) the coal is ground, mixed with oil, and injected into a converter at the high pressure of about 3500 lb. per square inch.   It is then heated to about 450°C. (842°F.) and treated with hydrogen at that temperature in the presence of catalysts.   The oils produced are separated by distillation.   The heavier fractions are used for mixing with the coal as charging stock.   The gasoline is ready for use after a slight treatment.   The intermediate oil is passed to the vapor-phase converters where it is mixed with hydrogen under pressure and heated to about 500°C. (932°F.).   This mixture of hydrogen and oil vapor then passes over a catalyst, where part is converted to gasoline and part to Diesel fuel.

Diesel fuels are produced also from the hydrogenation of carbon monoxide by the Fischer–Tropsch process.   It is reported (57) that the gas oil derived from Kogasin oil has a cetene rating of over 100.   A mixture of 40 per cent of this gas oil and 60 per cent of a tar oil had a rating of 56 cetene number (probably 54 to 55 cetane number).   Additional data on these two fuels are given in table 21.

The production of Diesel fuels by polymerization of olefins or alkylation of olefins and paraffins to produce paraffins can be accomplished when

[1] Private communication.

the economic needs justify.   To date, little thought has been given to the preparation of Diesel fuels by this method, chiefly because of the low price of Diesel fuel as compared to gasoline.   From a technical point of view, however, it appears that Diesel fuel of satisfactory quality for high-speed engines can be made by such a process, providing the chemical reactions involved are suitably controlled.   It has been found (20), for example, that in the presence of aluminum chloride as a catalyst and at about 50 atm. pressure (735 lb. per square inch) the reactions may be controlled to give products of any desired boiling range and chemical composition.   It is claimed also that paraffinic oils may be obtained without the use of a catalyst.

TABLE 21

Cetene rating and physical properties of Kogasin Diesel fuel (57)

PROPERTIES	GAS OIL	MIXED DIESEL FUEL
Cetene No	Over 100	56
Cetane No.*	100	54–55
Distillation characteristics:		
End point, °C. (°F.)		320 (608)
At least 60 per cent, °C. (°F.)	300 (572)	
Specific gravity (d_{20})	0.835–0 91	0 866
Viscosity at 20°C. (Engler)	<2 6	1 28
Flash point, °C. (°F.)	>65 (149)	68 (155)
Solidifying point, °C. (°F.)	<0 (32)	−16 (3)
Soluble alkali, per cent	<4	2
Water	<0 5	Free
Hard asphalt		0 02
Color		Brown

* Estimated by writers.

Another polymerization process has been suggested (75) in which paraffin wax is cracked to give unsaturated hydrocarbons.   This material is dewaxed, leaving unsaturated low-boiling liquid hydrocarbons.   These hydrocarbons are subjected to a polymerization reaction with a metallic halide catalyst such as zinc chloride, boron fluoride, and ferric chloride, to produce saturated higher-boiling hydrocarbons from which polymerized Diesel fuel of high cetane rating may be obtained by fractional distillation.

The possibility of lowering the pour point of a paraffinic Diesel fuel by mild cracking (79) has been investigated, with results as listed in table 22.

Dewaxing (79) also has an application for producing fuels of high ignition quality and low pour point.   Data for naphtha dewaxing of fuel oils are shown in table 23.

Pour-point depressors (79) have been found to be effective on Diesel fuels, particularly those with low pour points. This is illustrated in table 24.

TABLE 22

Effect of cracking on pour point and ignition quality (79)

Cracking temperature, °F		700	700	800	800
Cracking time, hours . . .	0	2	8	2	8
Cracking loss, per cent .	0	2	7	7	19
Resultant Diesel fuel:					
Ignition quality:					
Diesel Index No. .	63	62	54	57	50
Cetane No (delay) (45)	56	55	48	51	46
Pour point, °F . . .	35	0	−15	−5	−20

TABLE 23

Effect of dewaxing on ignition quality and pour point (79)

FUEL	POUR POINT	IGNITION QUALITY	
		Diesel Index No.	Cetane No. (45)
	°F.		
Original fuel:	55	73	69
Dewaxed .	0	62	55
Dewaxed	−30	58	51
Original fuel:	35	62	55
Dewaxed	0	58	51
Dewaxed	−30	53	48

TABLE 24

Use of Paraflow as a pour-point depressor for Diesel fuels (79)

PARAFLOW ADDED	POUR POINT				
per cent	°F.	°F.	°F.	°F.	°F.
0 0	50	35	10	−25	−40
0 1	50	30	5	−35	−50
0.5	40	15	5	−40	−60
1 0	40	15	0	−45	−80
3 0	35	5	−15	−75	−85

Acid treating (79) offers possibilities for producing fuels of high ignition quality, as shown in table 25.

Solvent refining (79) offers a method for the production of Diesel fuels. Representative data for extraction of straight-run and cracked fuels with sulfur dioxide are given in table 26. It will be noted that solvent

treating is not so effective with straight-run fuels as it is with cracked fuels. This conclusion may not be true for all types of solvents and Diesel oils. Although the "treating loss" (extract) appears large when extracting for the higher ignition qualities, it is not a total loss because the extract, which

TABLE 25

Effect of acid treating on ignition quality and pour point of cracked and straight-run Diesel fuels (79)

		CRACKED FUEL			STRAIGHT-RUN FUEL	
Acid, lb. per barrel ..	0	10	50	0	10	50
Treating loss, per cent	0	6	27	0	7	25
Diesel Index No .	45	48	55	38	41	48
Cetane No. (45) ..	42	44	49	39	40	44
Pour point, °F	−25	−25	−10	−50	−45	−30

TABLE 26

Effect of solvent treating on ignition quality and pour point (79)

Cracked fuel:				
Sulfur dioxide, per cent .	0	100	300	500
Yield (raffinate), per cent	100	76	59	44
Loss (extract), per cent	0	24	41	56
Diesel Index No	43	57	68	71
Cetane No. (45) . .	41	51	62	66
Pour point, °F .	−40	−35	−30	−5
Cracked fuel:				
Sulfur dioxide, per cent .	0	100	300	500
Yield (raffinate), per cent	100	75	57	41
Loss (extract), per cent	0	25	43	59
Diesel Index No	38	53	66	70
Cetane No. (45)	39	48	60	65
Pour point, °F ..	−50	−50	−35	−15*
Straight-run fuel:				
Sulfur dioxide, per cent .	0	100	300	500
Diesel Index No .	45	49	57	63
Cetane No. (45)	42	45	51	56
Pour point, °F . .	−25	−25	−20	0

* With the addition of 0.5 per cent of Paraflow, this −15°F. pour point was lowered to −50°F.

is aromatic in character, may be blended as tractor fuel or be recracked to produce gasoline of high antiknock value.

G. Solvent extraction of gasolines

Gasolines derived from the atmospheric distillation of crude oils in general contain paraffin hydrocarbons with straight chains predominating and

with naphthenes, aromatics, and sometimes olefins present. Cracked gasolines likewise contain varying percentages of these hydrocarbon groups, as illustrated in table 27.

The solvent extraction of motor fuels to segregate the low-octane fraction (raffinate) from the high (extract) is an effective means for increasing the volume of high-octane gasoline. The residue oil (raffinate) of low octane rating can be cracked into high-octane motor fuel. It is estimated that, if the 500 million barrels of motor fuel produced in the United States in one year (estimated 1937 production) were solvent-extracted, over 100 million barrels of gasoline having an octane number of 90 or over would result.

The Edeleanu process of extraction with sulfur dioxide for the separation of aromatics and olefins from the paraffins and naphthenes is in commercial operation, treating naphtha at the rate of 6000 barrels a day (66). A number of other units are operating, are projected, or are under construction at the present time (September, 1937).

TABLE 27

Chemical analysis of cracked motor fuels

PER CENT OF HYDROCARBONS	NORTHERN KANSAS TOPPED CRUDE OIL	KENTUCKY FUEL OIL	SMACK-OVER HEAVY CRUDE OIL	NORTHERN TEXAS FUEL OIL	LOST SOLDIER, WYOMING, CRUDE OIL	SPINDLE-TOP, TEXAS, CRUDE OIL
Unsaturates	16.1	14.4	14.7	16 0	11 7	14.7
Aromatics	17.8	22 5	27 5	18 6	15.9	17.3
Naphthenes .	12 8	10 0	21.2	11 7	14.5	32.6
Paraffins .	53.3	53 1	36.6	33 7	57.9	35.4

When extracting a Mid-Continent naphtha of 53° A.P.I. gravity, the yield of high-octane fuel varied from 9.1 to 12.5 per cent, as a function of the temperature of extraction which ranged from 0° to −60°F.; the results are shown in table 28.

A Sumatra naphtha when solvent-treated at 0°F. showed a 30 per cent yield of extract of 81.8 octane number, while at −40°F. the octane rating was 90.3 for a yield of 22 per cent. Detailed data are shown in table 29.

When solvent-extracting a South Texas naphtha of 57.9 octane rating, the yield of 80-octane fuel was 46.5 per cent at 0°F.; at −60°F., a 34 per cent yield of 90.8-octane product was obtained. The results are shown in table 30.

The properties of the raffinates derived from the extraction of Mid-Continent, South Texas, and Sumatra naphthas are shown in table 31.

The South Texas sulfur dioxide extract of 89.9 octane rating was separated into 20 per cent fractions and their properties determined as shown in

table 32. The last two fractions, representing 38 per cent of the extract, showed an octane rating of 99.5. When based upon the original South

TABLE 28

Extraction of straight-run Mid-Continent naphtha with sulfur dioxide (66)

	CHARGING STOCK	HIGH-OCTANE GASOLINE PRODUCED			
Experiment No		1	2	3	4
Sulfur dioxide used, per cent by volume		40	40	40	40
Extraction temperature, °F		0	−20	−40	−60
Yields, per cent by volume		12 5	10 6	9 6	9 1
Gravity, °A P I	53 1	36 7	34 7	33 5	32 2
Octane No., C.F R. motor method	Below 41	82 6	86 2	89 0	91 0
Unsaturates and aromatics, per cent by volume	9 5	70 7	78 6	84 3	89 1
Naphthenes, per cent by volume	15 6	7 3	5 9	4 8	3 4
Paraffins, per cent by volume	74 9	22 0	15 5	10 9	7 5
Sulfur, per cent by volume	0 03				0.10
Distillation characteristics:					
Initial boiling point, °F	225	243	251	251	255
10 per cent	256	271	276	275	279
50 per cent	301	309	313	313	314
90 per cent	359	362	362	361	364
End point, °F	397	412	413	414	414

TABLE 29

Extraction of straight-run Sumatra naphtha with sulfur dioxide (66)

	CHARGING STOCK	HIGH-OCTANE GASOLINE PRODUCED	
Experiment No		5	6
Sulfur dioxide used, per cent by volume		85	55
Extraction temperature, °F .		0	−40
Yields, per cent by volume		30.0	22.0
Gravity, °A.P.I ..	53 6	40 8	36 2
Octane No., C F.R. motor method		81 8	90 3
Unsaturates and aromatics, per cent by volume. .	19.8	61.6	78 7
Distillation characteristics:			
Initial boiling point, °F .	190	202	207
10 per cent . .	211	226	233
50 per cent	241	253	261
90 per cent . . .	288	293	296
End point, °F..	321	318	324

Texas naphtha, a yield of about 13 per cent of a motor fuel having an octane number of 99.5+ was obtained.

The comparative blending characteristics of a 91- and a 98-octane extract and isoöctane (2,2,4-trimethylpentane), in concentrations of 25, 50, and 75 per cent, are shown in table 33. The 91-octane number extract was obtained by treating the South Texas stock with 70 per cent sulfur dioxide at −60°F., as shown in table 30 under experiment 10. The

TABLE 30

Extraction of straight-run South Texas naphtha with sulfur dioxide (66)

	CHARGING STOCK	HIGH-OCTANE GASOLINE PRODUCED				
Experiment No		7	8	9	10	11
Sulfur dioxide used, per cent by volume		70	70	70	70	70
Extraction temperature, °F.		0	−20	−40	−60	0 to −60
Yields, per cent by volume		46.5	39.5	35.9	34.0	34.0
Octane No , C.F R motor method	57 9	80.0	84 4	88.2	91.1	90.8
Gravity, °A.P.I	46.8	38.9	36.5	35.0	33 7	33.6
Unsaturates and aromatics, per cent by volume	31 2	63.1	73.5	80.2	84.0	84.7
Naphthenes, per cent by volume	19.8	13.2	10.1	8.0	6.2	5.8
Paraffins, per cent by volume	49.0	23.7	16 4	11.8	9.8	9.5
Aniline point, °C.		−12 8	−17.7	−19.3	−19.3	−19.5
Sulfur, per cent by weight	Below 0.01	0.01			0.01	0.01
Freezing point, °F					Below −60	
Distillation characteristics:						
Initial boiling point, °F	232	239	237	241	247	247
10 per cent	256	258	259	261	267	267
50 per cent	292	290	288	289	292	292
90 per cent	344	338	336	336	337	336
End point, °F	382	398	390	390	394	391

98-octane number blending stock was produced by fractionation of another South Texas extract obtained at −60°F. A Mid-Continent straight-run naphtha, with an octane rating of 63.4 and boiling between 102° and 266°F., was used for the blending tests. Table 33 and figure 5 show the octane numbers of the respective blends in relation to the amounts of extract or isoöctane present. It will be noted that the blending value of

TABLE 31

Properties of raffinates produced by extracting straight-run naphthas with sulfur dioxide (66)

	ORIGIN OF NAPHTHA					
	Mid-Continent		Sumatra		South Texas	
Experiment No	1	4	5	6	7	11
Extraction temperature, °F	0	−60		−40	0	−60
Raffinates produced:						
Yields, per cent by volume	87.5	90 9	70 0	78.0	53.5	66.0
Gravity, °A P I	54 8	55 3	59 2	59.1	53 7	54 0
Octane No., C F.R motor method		Below 41	51 2	50	Below 41	Below 41
Unsaturates and aromatics, per cent by volume		1 5	2.0	1.2	3 5	1 3
Naphthenes, per cent by volume		16			24 5	25.1
Paraffins, per cent by volume		82.5			72.0	73.6
Distillation characteristics:						
Initial boiling point, °F	223		190		236	
10 per cent	255		211		259	
50 per cent	303		240		298	
90 per cent	362		292		350	
End point, °F	399		320		394	

TABLE 32

Fractionation of South Texas sulfur dioxide extract (66)

PROPERTIES	SULFUR DIOXIDE EXTRACT—VARIOUS CUTS					
	0–100 per cent	0–20 per cent	20–40 per cent	40–60 per cent	60–80 per cent	80–98 per cent
Gravity, °A.P.I	35 6	41.8	35 8	35 6	32.9	32.5
Doctor test	Sweet	Sweet	Sweet	Sweet	Sweet	Sweet
Unsaturates and aromatics, per cent by volume	78 2	53.2	81.3	82.0	92.7	92.0
Octane No., C.F.R. motor method	89 9	81 1	92.2	94.1	99.5+	99.5+
Distillation characteristics:						
Initial boiling point, °F	222	194	224	246	273	284
10 per cent	239	201	227	252	276	289
50 per cent	258	211	228	262	278	295
90 per cent	291	224	231	275	280	312
End point, °F	333	244	254	290	296	335

the 98-octane number extract compares favorably with isoöctane, and that the blending values of these extracts are about the same as their octane numbers.

Additional information on the subject of solvent extraction is given by F. W. Sullivan and O. FitzSimons. Sullivan (70) reports the use of a mixture of liquid carbon dioxide and sulfur dioxide as solvent upon a cracked naphtha boiling between 250° and 400°F. When solvent-extracted at −115°F., the cracked naphtha, containing 52 per cent of olefins, 47 per cent of paraffins and naphthenes, and 1 per cent of aromatics,
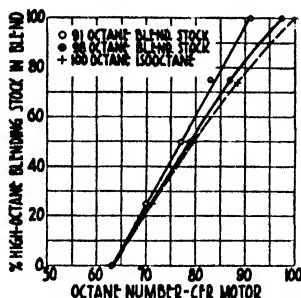
FIG. 5. Blending values of solvent-refined gasolines

TABLE 33

Octane numbers of various blends of extract and isoöctane with 63.4-octane straight-run gasoline (66)

PER CENT BLENDED WITH 63.4-OCTANE STRAIGHT-RUN GASOLINE	OCTANE NO. OF BLENDS		
	Sulfur dioxide extracts		Isoöctane
100	91.1	98 0	100
75	83.1	86.5	88.5
50	77.5	79.0	79.7
25	70.0	71.5	71.0
0	63.4	63 4	63.4

produced a fraction of 109 octane number (C.F.R. research method). FitzSimons (33) reports the use of a mixture of heterocyclic nitrogen bases, such as pyridine, quinoline, quinaldine, the picolines, the lutidines, etc. in conjunction with sulfur dioxide, for separation of the antiknocking from the knocking hydrocarbons in cracked naphthas rich in olefin hydrocarbons. When using a solvent mixture of 23 per cent pyridine and 77 per cent liquid sulfur dioxide, a yield of 28 per cent of extract of 103 octane number (C.F.R. research method) was obtained from vaporphase cracked naphtha.

III. MOTOR FUELS FROM NATURAL GAS

A. Natural gas as source

1. Methane, ethane, propane, and butanes: direct use as a motor fuel

Hydrocarbon gases are being used to an ever-increasing extent for motor fuel in the form of liquefied methane–ethane mixtures, propane–butane mixtures, or as butanes.   Methane–ethane mixtures are used to a limited extent, chiefly as fuel (not liquefied) for large stationary and "gas Diesel" engines.   In Germany and France a number of service stations are now selling liquefied methane–ethane as fuel for trucks and busses.   In the United States, liquefied propane–butane mixtures and butanes are used for tractors, trucks, busses, trains, construction and mine locomotives, power shovels, road graders, ditch diggers, industrial plant jitneys, oil well drilling, and in many other installations.

The volume of methane and ethane available during the year 1936 from natural and refinery gas was 2,475 billion cubic feet, of which 2,175 billion came from natural gas.[2]   This volume suggests a potential source of over 55 billion gallons of liquefied methane–ethane motor fuel.   The volume of propane and butanes available in the United States during 1936 from natural gases was approximately 8 billion gallons, from the distillation of crude oil about 1.5 billion, and from cracked gases about 4.5 billion gallons, or a total of over 14 billion gallons (34).   Thus the total volume of motor fuel potentially available from hydrocarbon gases in the United States during 1936 was over 69 billion gallons, or over three times as much gasoline as was consumed during that year.

Propane–butane mixtures, like methane–ethane mixtures, have advantages when used in the spark-ignition internal-combustion engine.   It is reported that compression ratios may be increased and higher thermal efficiencies obtained; better carburetion, not possible with a liquid fuel such as gasoline, is attained; dilution of lubricating oils is eliminated; very little carbon deposit results; the engine runs more smoothly and cooler with greater power output and better acceleration and idling; engine wear is reduced; spark plug life is lengthened; and obnoxious exhaust odors are eliminated (34).   Compression ratios with propane–butane or methane–ethane as fuel may be increased to as high as 9 to 1, depending upon combustion chamber design, size and speed of engine, and type of service. This increase in compression ratio is made possible by the high antiknock values of these gases, which range from 91 to over 125 octane number as shown in table 34.

The heating values of propane–butane and methane–ethane mixtures are considerably lower than those of regular motor gasoline on a B.t.u.

[2] Estimated by Gustav Egloff from references 2 and 58.

per gallon basis. However, because of the higher compression ratios possible with these gases, thermal efficiencies are higher, with the result that fuel consumption is about the same as with gasoline. The heating values for a number of liquid and gaseous fuels are shown in table 35. For comparative purposes, additional properties are included.

TABLE 34

Octane ratings of various hydrocarbon gases (23)

HYDROCARBON	OCTANE NO. C.F.R. MOTOR METHOD
Methane	125*
Ethane	125*
Propane	125*
Isobutane	99
n-Butane	91
Mixture: 30 per cent propane and 70 per cent butanes	105*

* Approximate ratings.

TABLE 35

Heating values and physical properties of various hydrocarbon fuels (liquid)

FUEL	BOILING POINT		GRAVITY AT 60°F.		VAPOR PRES- SURE IN LB. PER SQUARE INCH AT 100°F.	HEATING VALUE (GROSS)	
	°C.	°F.	Specific	°A.P.I.		B.t.u. per pound	B.t.u. per gallon
Methane*	−161.5	−258.7	0 247	440		23,910	49,250
Ethane*	−89.4	−129 0	0.410	213		22,040	75,380
Propane*	−42.2	−44.1	0.511	145	190	21,690	92,400
Isobutane*	−12.2	10.0	0.576	114	76	21,290	102,390
n-Butane*	−0.5	31.0	0.585	111	52	21,330	104,080
Aviation gasoline (34)			0.702	70		21,400	125,000
U. S. motor gasoline (34)			0.739	60		21,050	129,000
Kerosene (34)			0.816	42		20,000	135,000
Diesel fuel (34)			0.904	25		19,000	142,000

* Calculated from results of F. D. Rossini and G. B. Kistiakowsky, in Bureau of Standards Publications.

Methane–ethane and propane–butane mixtures, with their high volatility, do not present the problems of incomplete vaporization and unequal distribution which are commonly encountered with gasoline or other less volatile liquid fuels. Since these fuels are gases when they enter the carburetor and manifold, uniform distribution to all cylinders is assured and the difficulties occasioned by the wetting of the walls of the intake

manifold through condensation are eliminated. These characteristics add materially to the life of both the engine and the lubricants, since dilution of the oil in the crank case cannot occur from unvaporized fuel dropping from the pistons.

One of the most interesting applications of methane–ethane fuel is in the gas Diesel engine (59) which the city of Lubbock, Texas, installed in its lighting plant in 1936. The engine is substantially a standard Nordberg two-cycle air-injection Diesel. The gas, under pressure, enters the spray-valve cage exactly as does the injection air. When the spray-valve needle is lifted, the gas at 1100 lb. per square inch pressure (contrasted to the 500 lb. compression pressure in the engine cylinder) blows through the atomizer into the cylinder. Its high velocity, due to the pressure drop, insures proper diffusion and proper mixing with the air in the cylinder. According to reports (68), the operation of this gas Diesel engine has been excellent. The unit has carried its rated load without difficulty and handles variations in load with satisfaction. Cylinder wear has been about half the amount usually found in Diesel engines of the same size. The performance of this engine has prompted the Lubbock Light Department to order another Nordberg gas Diesel engine and to arrange for the conversion of another Diesel engine to the use of natural gas. There appear to be unusual possibilities in this new type of Diesel engine, particularly since it may be switched readily from gas to oil or from oil to gas as occasion dictates.

Liquid propane–butane applications are more numerous. Late in 1934, the city of Spokane, Washington, as a trial, converted ten busses of a fleet of one hundred thirty from gasoline operation to a mixture of propane and butane (16). This mixture consisted of 35 per cent of propane and 65 per cent of butanes. The experiment was found successful enough to warrant changing the entire fleet from gasoline to liquefied propane–butane. Over a two-year period a saving of 30 per cent in engine maintenance was reported (16).

The cost of converting a truck or bus to use liquefied propane–butane (5) varies from $75 to $200, depending upon the number and size of the fuel tanks installed and whether a change in compression is desired. In preparing this fuel for the engine, four distinct stages are required: namely, initial regulation, application of heat, final regulation, and carburetion. Because of the fact that the pressure of the propane–butane mixture might vary as much as 150 lb., initial regulation is necessary to reduce this variable pressure to a practically constant pressure of about 10 lb. per square inch. Heat is applied by means of an exchanger which utilizes the heat in the cooling-water system. Fuel is delivered from the heat exchanger as a gas under 10 lb. pressure to the final regulator. In many
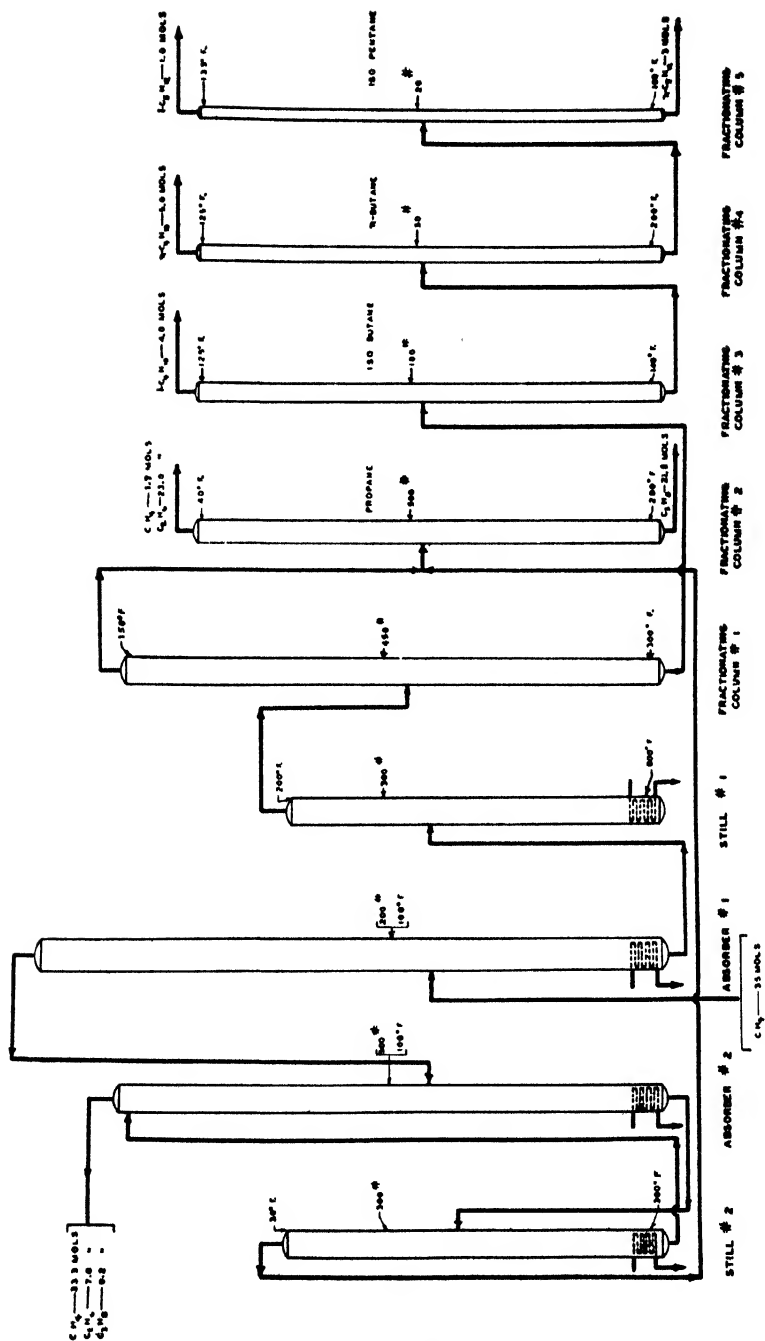
FIG. 6. Flow diagram of commercial process for separating hydrocarbon gases

cases, particularly in truck operation, it is often found desirable to provide for the use of gasoline as a stand-by fuel. In such cases, combination gasoline and propane–butane carburetors are installed.

Hydrocarbon gases, whether derived from oil wells, gas wells, the distillation of crude oil, or the cracking process, may be separated into their components,—methane, ethane, propane, butanes, and pentanes,—by compression, absorption, distillation, and stabilization. A schematic cutline of a commercial process used for this separation (76) is shown in figure 6. In this process, a natural gas having the composition shown in table 36 is separated into its components in the following manner. The gas is compressed at a pressure of 200 lb. while in contact with an absorption oil, such as mineral seal, at a temperature of 100°F. (absorber 1). The undissolved gas from the top of absorber 1 is compressed to a pressure of 500 lb. as it enters absorber 2. The gas leaving the top of absorber 2 consists

TABLE 36

Composition of sample of natural gas (76)

HYDROCARBON	MOLES
Methane	35
Ethane	30
Propane	22
n-Butane	5
Isobutane	4
n-Pentane	3
Isopentane	1

of 33.3 moles of methane, 7.0 moles of ethane, and 0.2 mole of propane. The oil from absorber 2 is discharged into still 2 at a pressure of 300 lb. and temperatures of 300°F. at the bottom and 30°F. at the top. The oil from absorber 1, containing dissolved gases, is pumped to still 1 at 300 lb. pressure where temperatures are maintained at 600°F. at the bottom and 200°F. at the top. The gaseous hydrocarbons from still 2 are compressed to a pressure of 500 lb. in fractionating column 2, where a top temperature of 40°F. and a bottom temperature of 200°F. are maintained. The gases from the top of fractionating column 1, which consist of a mixture of methane, ethane, and propane, are discharged into fractionating column 2 along with the gases from still 2 for the separation of the methane and ethane from the propane. The propane fraction from the bottom of column 2 is discharged to a storage tank after cooling. The gas recovered from column 2 contains 1.7 moles of methane and 23 moles of ethane. The purity of the propane fraction leaving the bottom of column 2 is 99.0

per cent, representing 21.8 moles of the 22 moles present in the original gas.

The butanes and pentanes discharge from the bottom of fractionating column 1 into column 3, where the isobutane is separated under 100 lb.

TABLE 37

Plant operating conditions for separation of hydrocarbon gases (76)

	PRESSURE	TEMPERATURE	
		Top	Bottom
	lb. per square inch	°F.	°F.
Absorber:			
No. 1	200	100	
No. 2	500	100	
Still:			
No. 1	300	200	600
No. 2	300	30	300
Fractionating column			
No. 1	450	150	300
No 2	500	40	200
No. 3	100	125	140
No. 4	50	125	200
No. 5	20	135	160

TABLE 38

Separation of hydrocarbon gases (76)

COMPONENT	ORIGINAL GAS	RECOVERY		FRACTIONATING COLUMN NO.
		Per cent	Moles	
	moles			
Methane	35	4 8	1 7	2
Ethane	30	76.7	23.0	2
Propane	22	99.0	21.8	2
Isobutane	4	100.0	4.0	3
n-Butane	5	100.0	5.0	4
Isopentane	1	100.0	1.0	5
n-Pentane	3	100.0	3.0	5

pressure at 125°F. The normal butane and the pentanes discharge from the bottom of column 3 into column 4, where the normal butane is separated from the pentanes at a pressure of 50 lb. and a top temperature of 125°F. The normal pentane and isopentane are discharged to storage tanks from the bottom of column 4 into column 5 at a pressure of 20 lb.

and a top temperature of 135°F., at which point the isopentane is separated from the normal pentane.

The operating conditions are summarized in table 37. The recovery of the various components in the gas under consideration is shown in table 38.

Typical analyses of a number of commercial hydrocarbon gases are shown in table 39.

TABLE 39

Typical analyses of natural (casinghead and gas-well) gases

DISTRICT	SAMPLE	PER CENT BY VOLUME OF						
		Carbon dioxide	Methane	Ethane	Propane	Isobutane	Normal butane	Pentanes and heavier
California (70):								
Kettleman Hills	Gas from field	0	81 60	8.47	5 29	0 78	2 03	1 83
North Belridge	Gas from field	1.1	92.21	3 05	1 77	0.28	0.92	0.67
Ventura Avenue .	Gas from field	0	89 49	3 34	3 64	0 78	1.32	1.43
Mountain View. .	Gas from field	0 9	75 84	5 45	7 82	2 0	3 83	4 16
Santa Fe Springs	Gas from field	1.3	68.69	12.16	10 42	1 65	3 35	2 43
Taft-Maricopa	Gas from field	14 2	64.97	5 14	5.72	1.72	3 10	5 15
Kettleman Hills	Absorption	0	83 59	8.68	5 42	0 80	1 48	0 03
North Belridge	plant dis-	1 1	93 49	3.09	1 79	0 28	0 67	0.01
Ventura Avenue	charge gas	0	91.20	3 40	3 71	0.79	0.88	0.02
Mountain View	(based on ex-	0.9	80.43	5.71	8.19	2 09	2.62	0 06
Santa Fe Springs	traction of	1.3	71.09	12.58	10.78	1 71	2 51	0 03
Taft-Maricopa	21.9 lb. Reid vapor pressure gasoline)	15 1	69.15	5 47	6 10	1 83	2.28	0.07
Texas (14):								
East Texas	Casinghead gas	0	41.40	15 80	24 20	2.80	9 70	6 10
Panhandle	Gas-well gas	0	87 13	5.83	4.25	0.55		2.22
Louisiana (14):								
Northern Louisiana	Combined casing- head and gas- well gas	0	92 53	3 85	1.57	1.57	1.09	0 96

2. Natural gasoline

Natural gasoline is an important part of our motor fuel supply, chiefly because of its high volatility, blending properties, and antiknock value, which ranges from 70 to 85 octane number. It is obtained from casinghead gas, which flows from oil wells along with the crude oil, and from gas-well gas. These gases contain hydrocarbons, such as methane, ethane,

propane, butanes, pentanes, hexanes, heptanes, and octanes, from which natural gasoline may be fractionated.

The presence of natural gasoline was first discovered (14) in the early 1880's, when many operators of natural-gas transportation systems experienced trouble with condensation in the lines. It was soon determined that this condensate was gasoline, and draw-off drips were installed in low places along the lines. At that time the facilities for collecting this so-called drip gasoline consisted in utilizing the normal gas line pressure with the addition of a few cooling coils.

Today, there are about eight hundred and fifty natural-gasoline plants in operation in the United States, with an estimated total daily capacity of over 10 million gallons (14). The greatest natural gasoline-producing area of the United States lies in the Mid-Continent and Gulf Coast fields. The actual production in the United States during 1936 amounted to 1,766 million gallons, or more than 8 per cent of the total U. S. motor fuel pro-

TABLE 40

Production of natural gasoline in the United States (73, 14) for the years 1916–1936

YEAR	MILLION GALLONS	PER CENT OF TOTAL MOTOR FUEL PRODUCTION
1916	103	5
1920	385	7
1925	1,127	10
1930	2,210	12
1935	1,632	8
1936	1,766	8

duction (73). In 1916 the volume was 103 million gallons, or about 5 per cent of the total (14). Production for the intermediate years is shown in table 40.

When natural gasoline is the primary product desired from casinghead or gas-well gas, its separation from methane, ethane, and propane is much simpler than when individual components are the desired products. This separation may be accomplished by: (1) simple compression and stabilization; (2) compression followed by absorption and fractionation, or absorption, distillation, and fractionation; (3) absorption in activated carbon followed by distillation and stabilization. This process is now largely superseded by the other processes mentioned.

The simplest method is shown in the flow diagram of figure 7, which utilizes compression of the gases followed by stabilization of the gasoline produced to the desired vapor pressure (15). The gas is compressed to 250 lb. per square inch, after which it is cooled to 75°F., run to a surge tank

for intermediate storage, and then to the stabilizer shown.   The bottom portion of the stabilizer or fractionator is maintained at a temperature of 250°F., while the top temperature is held at 110°F. by recirculation
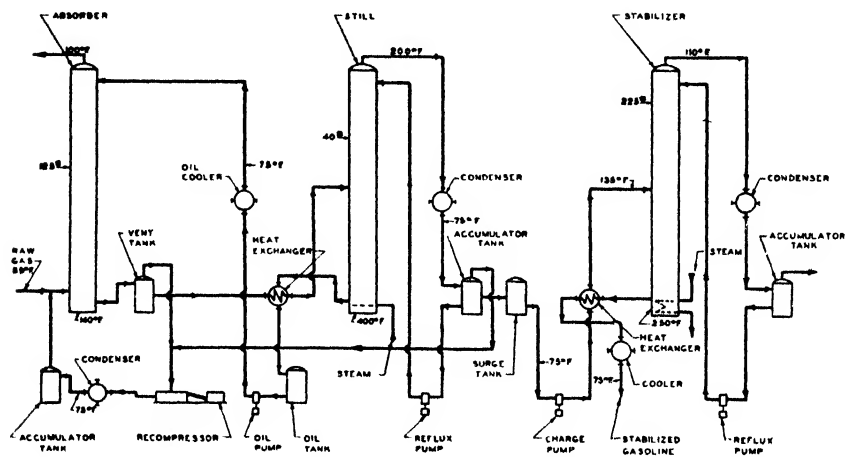
FIG. 7. Flow diagram of method (compression, followed by stabilization) for extracting gasoline from hydrocarbon gases.
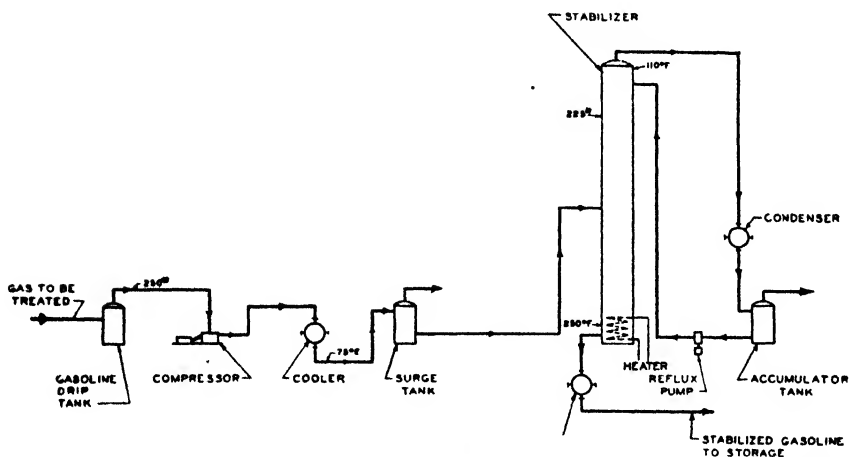
FIG. 8. Flow diagram of method (compression, followed by absorption and fractionation) for extracting natural gasoline from hydrocarbon gases.

of the liquid in the accumulator tank.   The pressure is maintained at 225 lb.

Another method for producing natural gasoline is shown in figure 8. The gas is first compressed; this is followed by absorption in a solvent such

as mineral seal oil; the gasoline is then distilled and finally stabilized to the desired vapor pressure (15).

For commercial purposes natural gasoline is defined by the following specifications:

Reid vapor pressure at 100°F	10-34 lb. per square inch
Per cent evaporated at 140°F	25-85
Per cent evaporated at 275°F .	Not less than 90
End point . . .	Not higher than 375°F.
Corrosion	Non-corrosive
Doctor test	Negative (sweet)
Color . . .	Not less than +25 (Saybolt)

Typical analyses of natural gasoline as produced in the Mid-Continent and Gulf Coast fields are given in tables 41 and 42.

When reducing natural gasoline from the various sources to three groups, it is obvious that considerable leeway must be allowed in octane rating

TABLE 41

Typical analyses of Mid-Continent and Gulf Coast natural gasoline (14)

PROPERTIES AND COMPOSITION OF GASOLINE	SOURCE OF GASOLINE			
	East Texas		North Texas	
Reid vapor pressure, lb per square inch at 100°F.	26	18	26	18
Gravity, °A P.I	91 0	86 4	87.5	82.5
Distillation characteristics:				
Per cent evaporated at 100°F .	55.0	33.0	40.0	27.5
Per cent evaporated at 140°F	85.0	77.5	72.5	65.0
Per cent evaporated at 212°F . . .	96.0	95 5	92.5	91.5
End point, °F . . .	304	309	315	320
Octane No., C.F.R. motor method . .	84	78	82	75
Hydrocarbon composition, volume per cent:				
Propane			0.08	
Isobutane . . .	1 23		1 54	1.04
n-Butane .	35.26	14.42	30.95	14.05
Isopentane . .	24.15	31 66	10.59	13.25
n-Pentane . .	20.37	28.06	20.25	25.45
Hexane . .	10.22	13.97		
Hexane plus .	8.77	11.89	36.59	46.21

and specific hydrocarbons present. It will be noted that as front-end volatility increases so does the octane rating. However there are a few plants, principally in the Gulf Coast area, which produce a product of relatively low volatility but of high octane rating. Examination shows this to be due to the presence of aromatics, naphthenes, and certain branched-chain paraffins (14).

TABLE 42

Typical analyses of Mid-Continent natural gasoline of low, medium, and high volatility (14)

PROPERTIES AND COMPOSITION OF GASOLINE	VOLATILITY			VOLATILITY		
	Low	Medium	High	Low	Medium	High
Reid vapor pressure, lb per square inch at 100°F	26	26	26	18	18	18
Gravity, °A.P.I	78–82	82–85	84–90	77–81	80–84	84-88
Distillation characteristics:						
Per cent evaporated at 100°F	5–10	20–30	30–45	5–10	15–25	30–40
Per cent evaporated at 140°F	35–45	55–70	70–85	30–40	50–65	68–80
Per cent evaporated at 212°F	70–80	85–92	93–97	70–80	82–90	91–96
End point, °F	365	347	329	365	347	329
Octane No., C.F R motor method	Up to 72	74–78	80–85	65–70	71–74	75–78
Hydrocarbon composition, volume per cent:						
Butanes				18–20	16	15
Pentanes				25–30	35–40	55–60
Hexanes plus				50–57	44–49	25–30

TABLE 43

Octane ratings and physical properties of various straight-chain and branched-chain paraffin hydrocarbons contained in natural gasoline

HYDROCARBON	OCTANE NO BY C.F R MOTOR METHOD	GRAVITY AT 60°F.		BOILING POINT	
		Specific	°A.P.I.	°C.	°F.
Butanes:					
Isobutane	99	0 5665	119 3	−10 2	13.6
n-Butane	91	0 5824	110.7	0.6	33.8
Pentanes:					
2,2-Dimethylpropane	83	0.631 D		9.5	49 1
Isopentane	90	0 621 $D^{19\ 1°}$	94.9	28.0	82.3
n-Pentane	64	0.631 $D^{20°}$		36 2	97.2
Hexanes:					
2,3-Dimethylbutane	95	0.6612 $D^{20°}$		58.1	136.6
n-Hexane	59	0 66 $D^{20°}$		69 0	156.2
Heptanes:					
2,2-Dimethylpentane	93	0.674 $D^{20°}$		78.6	173.5
2,3-Dimethylpentane	85	0.6950		89.4	192.9
2,4-Dimethylpentane	90	0.681 $D^{20°}$		83.9	183 0
2-Methylhexane	64	0.707 $D^{20°}$		90.4	194.7
n-Heptane	0	0.684 $D^{20°}$		98.4	209.1
Octanes:					
n-Octane	−28	0.707 $D^{15°}$		124 6	256.3
2,2,3-Trimethylpentane	101	0.722 $D^{15°}$		110.8	231.4
2,2,4-Trimethylpentane	100	0.704 $D^{15°}$		99.3	210.7

As indicated in tables 41 and 42, the hydrocarbons present in natural gasoline are predominantly straight-chain and branched-chain paraffins.
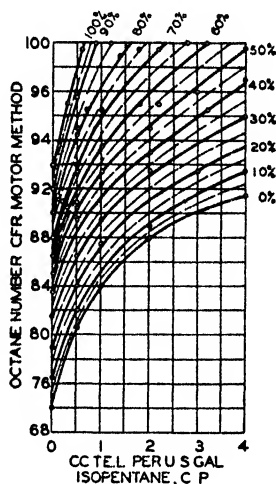
FIG. 9. Isopentane blended with 70-octane straight-run gasoline, with and without addition of tetraethyl lead.
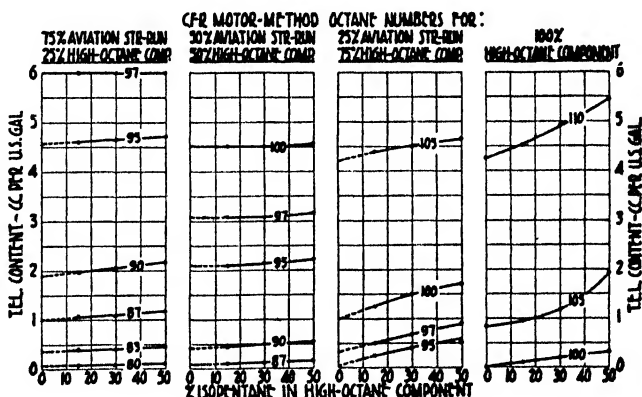
FIG. 10. Isopentane blended with isoöctane and aviation straight-run gasoline, with and without addition of tetraethyl lead.

The octane ratings and physical properties of a number of these individual hydrocarbons are shown in table 43.

One of the principal constituents of natural gasoline is isopentane. It is estimated that by simple fractionation 190 million gallons of isopentane could be produced annually in the United States (62). Its high antiknock

value (90 octane number), good susceptibility to tetraethyl lead, and low boiling point (82.3°F.) make it an excellent blending agent for high-octane aircraft fuels   These properties are illustrated in figures 9 and 10.

In the production of 100-octane aircraft fuel, isopentane is generally blended with the main components, isoöctane and straight-run gasoline, for the purpose of supplying the required front-end volatility.   The amount of isopentane added is usually restricted to about 15 per cent, because of its relatively high vapor pressure.   This is illustrated in table 44, wherein 100-octane isooctane, 74-octane aviation straight-run gasoline of 7 lb. Reid vapor pressure, and isopentane are blended to produce 100-octane fuel with 3 cc. of tetraethyl lead per gallon.

TABLE 44

Composition of 100-octane fuel containing 3 cc. of tetraethyl lead per gallon (62)

ISOPENTANE	AVIATION GASOLINE	ISOÖCTANE	REID VAPOR PRESSURE
per cent	*per cent*	*per cent*	*lb per square inch at 100°F.*
0	38.0	62 0	4.0
10	37.2	52.8	5.8
17	36.7	46 3	7.0
20	36.4	43 6	7.7
30	35 7	34 3	9 5
40	34.9	25.1	11.4
50	34.1	15 9	13.3

IV. MOTOR FUELS FROM CRACKED GASES

A. *General*

Hydrocarbon gases, such as propane, propene, butanes, and butenes, derived from natural gas and petroleum, present a potential yearly output of 9 billion gallons of motor fuel ranging from 76 to 100 octane number (24).

The methods used for converting these gases into high-octane motor fuels are thermal and catalytic polymerization (24).   The thermal method produces aromatic and olefinic types of motor fuels at high temperatures and high and low pressures, whereas the catalytic method operates at comparatively low temperatures and pressures and produces an olefinic type gasoline.   If desired, the catalytic method can be controlled so that when the butenes are polymerized and hydrogenated an isoöctane gasoline of 90 to 100 octane number results.

The octane ratings of a number of pure olefin hydrocarbons are shown in table 45.

Thermal and catalytic polymerization methods are now in commercial use,—namely, the "unitary" and "multiple-coil" thermal methods and

the UOP catalytic method. The daily production of polymer gasoline, including those units under construction (August 1, 1937), is over 1,300,000 gallons of gasoline ranging in octane number from 76 to 100.

B. Thermal polymerization

The unitary thermal process (24, 49) converts hydrocarbon gases at high temperatures and pressures into liquids ranging in properties from gasoline to gas oil. In this process, which is owned by the Polymerization Process Corporation, gaseous olefins and paraffins are treated at temperatures between 800°F. and 1100°F. and pressures ranging from 800 to 1200 lb. per square inch. The gasoline derived from this process has an octane rating of 76 to 79, depending upon the charging stock and operating conditions of the plant. The use of feed stocks high in unsaturates (65 to 70 per cent) results in a product in which aromatics and monoolefins appear to be predominant. The products obtained from feed stocks lower in unsaturates (30 to 38 per cent) are more paraffinic than aromatic or olefinic, and a considerable portion of the paraffins is isoparaffins. Production by this method is at the rate of 10,000 barrels of gasoline per day.

A flow chart of the unitary process is shown in figure 11.

The results obtained by processing a stabilizer reflux on a recycling basis are given in table 46.

Inspection data on typical products from processing various representative feed stocks by the unitary polymerization process are given in table 47.

In the multiple-coil process (24, 18) the operation consists of first treating cracking plant gas at temperatures of 900–1000°F. and pressures of 600–800 lb. per square inch. The liquids derived from this operation are withdrawn and the gaseous portion, which consists of the residue paraffins, is subjected to further cracking at 1300°F. for production of olefins. The olefinic gas from this operation is treated at temperatures of 1150–1300°F. and pressures of 50–75 lb., producing gasoline, fuel oil, and tar. In the high-temperature operation, a gasoline of 85 to 105 octane rating is obtained. At the lower temperatures the octane rating of the polymer gasoline is between 78 and 80.

The process is owned by the Pure Oil and Alco Products Companies. Daily production amounts to 2800 barrels. A flow chart of the process is shown in figure 12.

The results obtained from three types of hydrocarbon gases by the multiple-coil process are shown in tables 48 to 52 inclusive.

C. Catalytic polymerization

The UOP catalytic polymerization process (24, 22), which is owned by the Universal Oil Products Company, operates on olefin-containing gases.

TABLE 45

Octane ratings and physical properties of pure olefins

OLEFIN	BOILING POINT		GRAVITY AT 60°F.		OCTANE NO., C.F.R. MOTOR METHOD	OCTANE NO., C.F.R. RESEARCH METHOD BLENDING (35)
	°C	°F	Specific	°A.P.I.		
Ethylene	−103.9	−156.0	0.410	213.0		86
Propene	−47.7	−54.0	0.526	138.0		102
1-Butene (23)	−6.1	21.0	0.600	104.0	80	112
2-Butene (23)	+1.5	33.9	0.613	99.0	83	
Isobutene (23)	−6.6	20.0	0.597	105.0	87	
Diisobutene					84	
Triisobutene					87	
Diisopentene					75	
2,2,4-Trimethyl-3-pentene (9)	102.6	216.68	0.715		89	144
2,2,4-Trimethyl-4-pentene (9)	101.2	214.16			86	150
α-Isononene (9)	141.5–143.0	286.7–289.4			75	
β-Isononene (9)	143.0–145.0	289.4–293.0			84	
1-Pentene	40.0	104.0	0.652	85.4		99
2-Pentene	38.39	101.1	0.667	80.8		
α-Isoamylene	25.0	77.0	0.653	85.3		
β-Isoamylene	36.39	97.5	0.656	84.3		125
2-Methyl-2-butene	38.4	101.12	0.668			157
2,3-Dimethylbutadiene	68.8–68.9	155.84–156.02	0.7264 $D^{68°}$			212
3-Methyl-2-pentene	65.7	150.26	0.722			109
2,4-Hexadiene	82.0	179.6	0.718			174
1,5-Hexadiene	60.0	140.0	0.688			79
1-Hexene	64.1	147.38	0.683			85
2-Hexene	67.9	154.22	0.6813 $D^{68°}$			100
1-Heptene	99.0	93.7–93.8 at 771 mm.	0.6993 $D^{68°}$			55

3-Heptene	95.8	204.44	0 7016 D⁶⁸°	95

3-Heptene	95.8	204.44	0 7016 $D^{68°}$	95
3-Ethyl-2-pentene	98.0	208.4	0.725	124
2,2-Dimethyl-4-pentene	76 0- 76.1	168 8 -168.98	0 6881 $D^{68°}$	147
2,3-Dimethyl-2-pentene	95.1	203 18	0 719	127
2,4-Dimethyl-2-pentene	84.0	183.2	0 699	122
2-Methyl-5-hexene	84 7	184 46	0 6936 $D^{68°}$	83
3-Methyl-5-hexene	87 2- 87.5	188 96-189.5	0 6969 $D^{68°}$	86
2,2,3-Trimethyl-3-butene	77.8- 77 2	170.96-172.04	0 7023 $D^{68°}$	132
1-Octene	121.85 at 765 mm.	251.24	0 7158 $D^{68°}$	25
2-Octene	123 2-123.7	253.76-254.66	0 722 $D^{68°}$	55
3-Octene	122 7-122.9	252 86-253 22	0 7185 $D^{68°}$	73
4-Octene	122.0-122.3	251 6 -252 14	0 7184 $D^{68°}$	91

* Calculated blending value = 25 per cent in 50-octane straight-run reference fuel.

The sources of these gases may be either the cracking process or the catalytic dehydrogenation or cracking of propane and butanes to their corresponding olefins.

POLYMER GASOLINE
(Polymerization Process Corp Process)
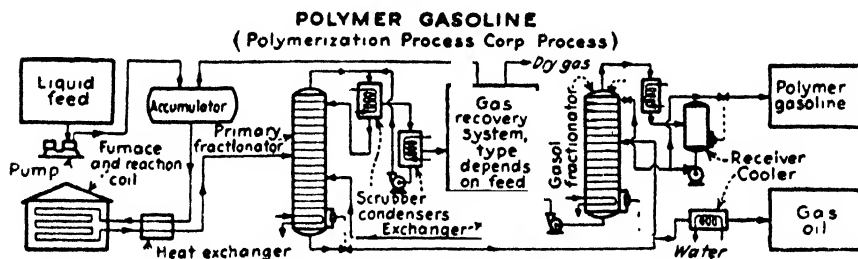
FIG 11. Flow diagram of "unitary" polymerization process

TABLE 46

Stabilizer reflux (recycling operation) (24, 49)

Pressure, lb per square inch	800	1200	1200	1200
Temperature, °F	1000	1000	1100	1030
Net yield, per cent by weight	67 9	69 0	69 6	64 5
Saturates in feed (net), per cent by weight	57 0	54 0	60 7	59 9
Unsaturates in feed (net), per cent by weight	43 0	46 0	39 3	40 1
Net yield, per cent unsaturates in fresh feed	158	150	177	161
Gallons liquid per 1000 cu ft .				
Net gaseous feed	12.78	13 10	14 40	13 5
Gross feed, per cent by volume:				
Ethylene	3.4	1.9	2 4	2 0
Ethane	12.2	6 8	9 0	6 5
Propene	29 6	30 5	21 3	21 0
Propane	46 3	49 8	38 8	39 6
Butene	4 3	4 8	11 0	13 6
Butane	4 2	6 2	16.9	17 3
Net feed, per cent by weight:				
Propene	43 0	41 1	23 1	20.3
Propane	57 0	54 0	36 4	37 1
Butene		4 9	16 1	19 8
Butane			24 3	22 8
Octane No , C.F.R. motor method:				
Blending value, 50 per cent in fuel A-3*	92	90	83	88

* Octane No. = 43.6.

The distinctive property of cracked gas is its content of unsaturated hydrocarbons. By regulation of the cracking process (time, temperature, and pressure) the percentages of the different hydrocarbons may be varied considerably. The quality of cracked gases is shown in table 53.

TABLE 47

Pilot plant and commercial plant operation (24, 49)

PROPERTIES	PRODUCT FROM PILOT PLANT OPERATION WITH STABILIZER REFLUX		PRODUCT FROM COMMERCIAL PLANT ON BUTANE FEED
	Raw product†	Clay-treated	Clay-treated
Gravity, °A.P.I	65 1	66.5	61.4
Distillation characteristics:			
Initial boiling point, °F	100	105	95
10 per cent	123	126	120
20 per cent	134	134	133
50 per cent	164	161	180
90 per cent	296	258	361
End point, °F	414	314	449
Octane No., C.F.R. motor method:			
Straight			79
Blending value, 50 per cent in reference fuel A-3*	92	90	
Reid vapor pressure, lb per square inch at 100°F.	10 7		
Color		30+	30+
Color after 8 hr. in sun		30+	
Copper-dish gum, mg		10 4	
Induction period, min			120

* Octane No = 43.6.

† Cut to 329°F. end point before clay-treating; treating loss, 1 per cent.

POLYMER GASOLINE
(Pure Oil - Alco Multicoil System)

Key F, Furnace, R.Reaction coil, J,Chilling jet; T,Tar separator, C.Condenser; A.Accumulator
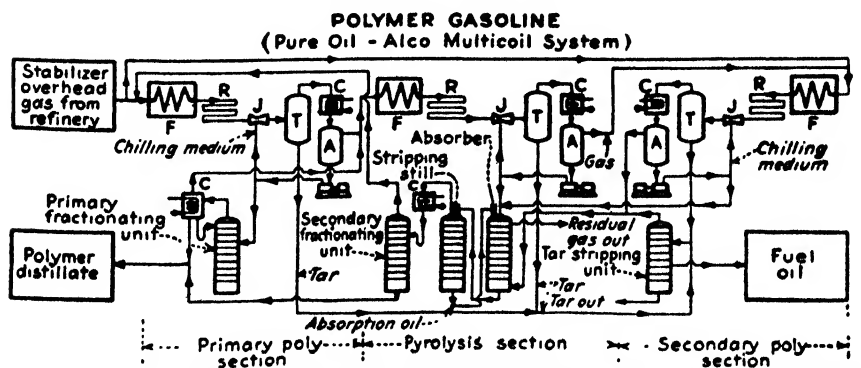
FIG. 12. Flow diagram of "multiple-coil" polymerization process

In this process the gases are heated to about 450°F., under 200 lb. pressure, in a pipe-coil heater from which they flow to catalyst chambers

containing solid phosphoric acid. The reaction is exothermic, a temperature rise of about 150°F. taking place in the catalyst bed. The polymer gasoline vapors pass through a cooling coil and thence to a receiver. The gasoline is pumped to a stabilizer in order to produce a product of the

TABLE 48

Typical analysis of Gyro vapor phase residue and stabilizer overhead gases (24, 18)

CONSTITUENT	RESIDUE GAS	STABILIZER OVERHEAD
	mole per cent	*mole per cent*
Methane and hydrogen	32.5	0.5
Ethylene	23 9	9 2
Ethane	13.4	8.3
Propene	16 8	40 3
Propane	4 9	10 4
Butene	6.1	28 4
Butane and heavier	2 4	2.9

TABLE 49

Typical operation with residue gas (24, 18)

Charging stock:	
Specific gravity	1.06
Unsaturates, per cent	47.2
Yields of products:	
Treated gas:	
Cu. ft. per cubic foot of charge	0.80
Specific gravity	0.87
Unsaturates, per cent	18.4
Liquid:	
Gal. per 1000 cu. ft. of charge	4.4
End-point gasoline:	
Gal. per 1000 cu. ft. of charge	3.7
Gravity, °A.P.I	52.4
Total liquid, per cent	84
Distillation characteristics:	
Initial boiling point, °F	96
10 per cent	134
50 per cent	220
80 per cent	320
End point, °F	420

desired vapor pressure. The polymer product as produced has an octane rating of 80 to 83.

The residue gas from the stabilizer is made up substantially of propane and butanes. These paraffin hydrocarbons may be dehydrogenated

TABLE 50
Typical operation with stabilizer overhead gas (24, 18)

Once-through operating conditions:	
Temperature of coil outlet, °F	1175
Pressure of coil outlet, lb. per square inch gage	55
Conversion, per cent	80
Charging stock:	
Specific gravity	1.352
Unsaturates, per cent	79.6
Yields of products:	
Treated gas:	
Cu. ft. per cubic foot of gas charged	0.46
Specific gravity	0.86
Unsaturates, per cent	34 5
Liquid:	
Gal. per 1000 cu. ft.	98
End-point gasoline:	
Per cent boiling up to 350°F	68
Gravity, °A.P.I	26 4
Octane No., C.F.R. motor method	86
Distillation characteristics:	
Initial boiling point, °F	120
10 per cent	172
30 per cent	190
50 per cent	204
90 per cent	267
End point, °F	352

TABLE 51
Typical operation with absorber gas (24, 18)

Once-through operating conditions:	
Temperature of coil outlet, °F	1275
Pressure of coil outlet, lb. per square inch gage	60
Conversion, per cent	37.4
Charging stock:	
Specific gravity	0 79
Unsaturates, per cent	39.4
Yields of products:	
Treated gas:	
Cu. ft. per cubic foot of gas charged	0.85
Specific gravity	0.72
Unsaturates, per cent	0.29
Liquid:	
Gal. per 1000 cu. ft.	1.75
Gravity, °A.P.I	21.6
End-point gasoline:	
Per cent boiling up to 350°F	76
Octane No., C.F.R. motor method	102

TABLE 52

Typical operation with liquid feed (using higher molecular weight constituents only) (24, 18)

Commercial plant handling 4,050,000 cu. ft. per day; average operation, September 1 to 20, 1934

Charging stock (including recycle):	
Specific gravity	1.51
Unsaturates, per cent	49 4
Conversion of unsaturates, per cent	86 7
Recycle ratio	1 75
Yields of products:	
Fuel oil:	
Gal. per 1000 cu. ft. of fresh charge	3.0
Gravity, °A.P.I..	8.0
Treated gas:	
Specific gravity	1.01
Unsaturates, per cent	22.0
End-point gasoline:	
Gal. per 1000 cu. ft. of fresh charge	8 8
Gravity, °A.P.I	55.0
Octane No., C.F.R. motor method	76.0
Distillation characteristics:	
Initial boiling point, °F	90
10 per cent	105
30 per cent	145
50 per cent	182
90 per cent	323
End point, °F	398

TABLE 53

Typical analyses of cracked gases

| DISTRICT	PER CENT BY VOLUME									
	Methane	Ethane	Propane	Butanes	Pentanes	Ethylene	Propene	Butenes	Hydrogen	Carbon dioxide, etc.
Mid-Continent (23):										
Receiver gas	22 2	17 3	26 8	5.6	0.2	6 0	11 2	4 0	4 3	2 4
Stabilizer reflux	0.1	3.2	16.8	40.5	1.2	0 6	16.6	20 2	0 1	0.7
Stabilizer gas	3 4	17 8	22 2	2 0	0 2	16 0	29.0	4.9	0.6	3.9
Lean gas		20 2	18.0	7.1		4.7	7.5	4.2	35 4	2 9
"BB" fraction				51.9				44.0	2.5	1.6
Michigan (5):										
Stabilizer reflux	0	3.2	18 5	23.4		0.3	11.9	42.7	0	0
Stabilizer gas	0	3.4	26.6	17 9	0 3	1.9	16.4	33 5	0	0
Lean absorber gas	20.4	25.4	16.3	5.3	1.2	6.2	13.6	6.1	4.1	1.4
Receiver gas	16.2	22.8	15.8	5.7	6.4	6.0	13.4	9.2	3.4	1.1
Total gas	14.5	18.0	15.7	9.6	0.7	5.1	20.7	6.0	3.8	5.9
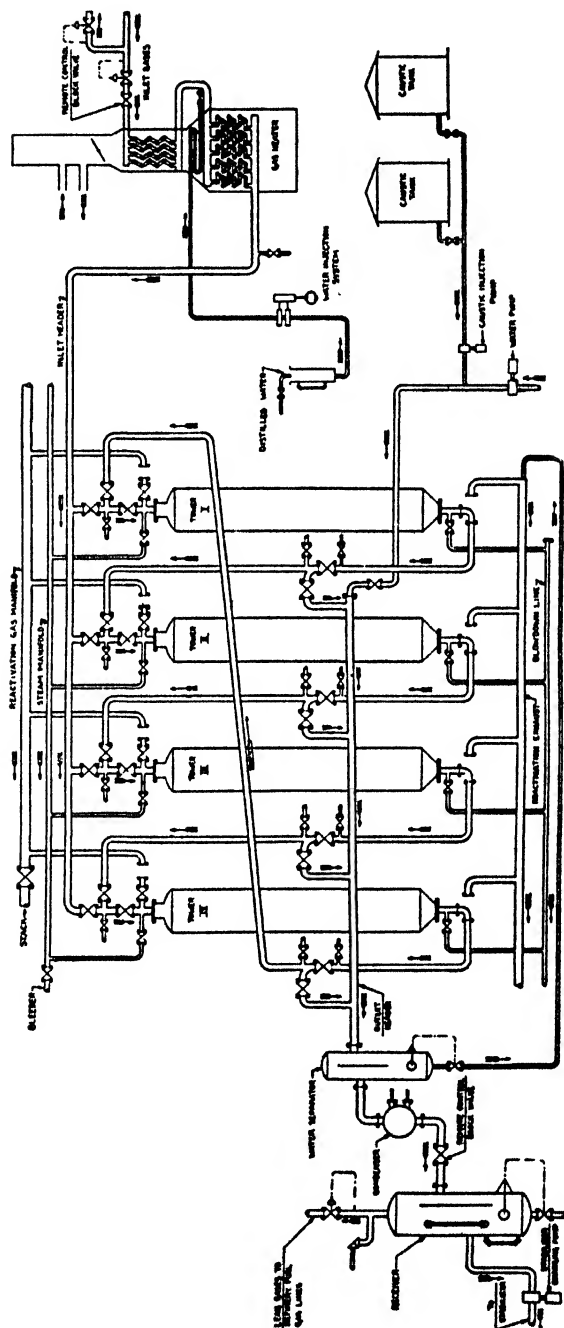
Fig. 13. Flow diagram of "UOP Catalytic" polymerization process

catalytically to olefins, or cracked to olefinic gases, and then pumped to the catalytic polymerization unit and processed exactly the same as the original gases

A flow diagram of the UOP catalytic polymerization process is shown in figure 13.

Experimental data, using stabilizer gas from typical vapor-phase and liquid-vapor-phase cracking as charging stock, are shown in table 54. With this particular gas, the yield of polymer gasoline having a Reid vapor pressure of 10 lb. per square inch was 6.5 gallons per 1000 cu. ft. By catalytic dehydrogenation of the gas leaving the polymerization plant,

TABLE 54

Operation of catalytic polymerization process (24, 22)

CHARGING STOCK AND YIELD OF GASOLINE	VAPOR-PHASE CRACKED GAS	LIQUID-VAPOR-PHASE CRACKED GAS
	mole per cent	*mole per cent*
Charging stock:		
Methane	26 5	8 6
Ethane–ethylene	29.5	13 0
Propene	18.6	14.0
Propane	8 2	34.4
Butenes	9 4	10 2
Butanes	2.4	18 2
Pentenes	4 0	1 6
Yields of gasoline,* gallons per 1000 cu. ft.:		
Catalytic polymerization only	6 5	4 6
Catalytic dehydrogenation and polymerization of polymer unit residue gas	2 2	10 7
Polymerization and dehydrogenation operation:		
Base on total gas charged	8.7	15 3
Based on C_3–C_4 fraction..	19.7	19 5

* Reid vapor pressure = 10 lb. per square inch.

followed by catalytic polymerization, an additional yield of 2.2 gallons per 1000 cu. ft. was obtained, making a total yield of 8.7 gallons of polymer gasoline. This is equivalent to 19.7 gallons per 1000 cu. ft. based on the C_3–C_4 (propane–propene and butanes–butenes) fraction.

The catalytic polymerization process may also be carried out to polymerize selectively the normal butene and isobutene present in the gases to isooctenes which, on hydrogenation, yield isooctane gasoline of 90 to 100 octane number. It is estimated that there are over a billion gallons of this isooctane fuel potentially available yearly from the hydrocarbon gases in the United States. This is assuming that the butanes in natural and refinery gases are catalytically dehydrogenated to butenes, then poly-

merized to isooctenes, and finally hydrogenated to isooctanes   Production
by the UOP catalytic polymerization process, when all units are in opera-

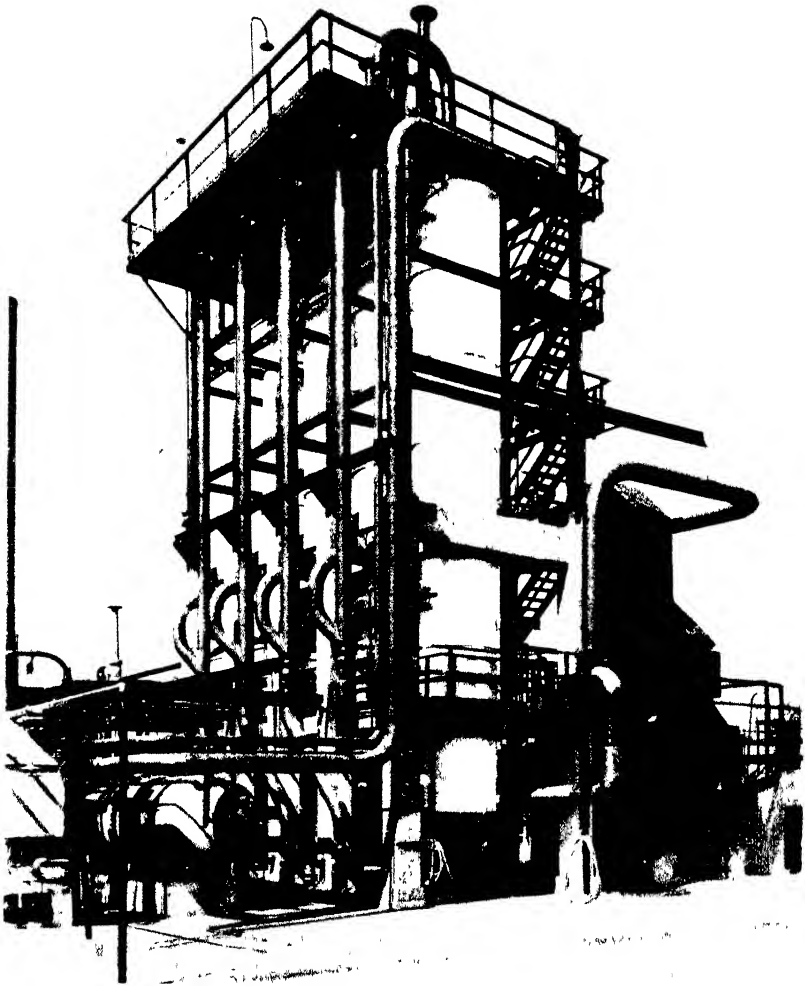FIG 14 Catalytic gas polymerization unit of the Universal Oil Products Company, handling eight million cubic feet of gas per day

tion, is at the rate of 16,500 barrels per day, of which 6000 barrels are
isooctane gasoline

Laboratory data, octane ratings, and octane blending values of gasolines
produced commercially by the three polymerization processes described

TABLE 55

Laboratory inspection data and octane blending values of various polymer gasolines, isooctanes, and benzene

GASOLINE	GRAVITY, °A.P.I.	DISTILLATION CHARACTERISTICS, °F							OCTANE NO. OF BLENDS OF HIGH-OCTANE FUEL IN REFERENCE FUEL A-3*								OCTANE BLENDING VALUE OF BLENDS OF HIGH-OCTANE FUEL IN REFERENCE FUEL A-3†							
		Initial boiling point	10%	20%	30%	50%	90%	End point	5%	10%	15%	20%	25%	50%	75%	100%	5%	10%	15%	20%	25%	50%	75%	100%
Polymer gasoline																								
Unitary polymer (49)	54.7	101	146	163	208		339	402	47.0	49.5	52.0	54.5	56.0	74.0		82	112	105	101	97	95	88	85	82
Multiple-coil (18)																								
High-pressure polymer†	31.5	169	195	202	225		324	392	47.0	49.5	52.0	54.5	56.0	71.0		73	112	103	99	96	95	88	80	73
High-octane polymer†									46.5	49.5	52.0	55.0	58.0	70.0	82.5	94	102	103	99	103	101	96	96	94
Catalytic																								
Regular polymer	67.0	101	156	178	212		314	408	48.0	52.0	55.5	59.0	62.5	67.0	73.5	82	132	128	123	123	119	103	91	82
Selective polymer	61.4	190	221	225	228		235	280	48.0	52.0	56.5	60.0	64.0	77.0	82.0	84	132	133	130	126	124	110	95	84
Diisobutene	64.5	212	213	214	215		216	238	49.0	54.0	58.0	62.5	66.0	77.0	82.0	84	152	153	143	138	133	111	95	84
Isooctane gasoline																								
Hydrogenated selective polymer	66.6	188	218	222	226		238	273	46.0	48.5	51.0	53.0	55.5	69.5	83.0	95	92	93	93	91	91	91	95	95
Hydrogenated diisobutene	71.0	206	208	209	210		213	244	46.0	48.5	51.0	53.0	56.5	70.5	84.5	99	92	92	96	93	95	97	98	99
Benzene (commercial)	29.3	173	174	174	175		175	212	45.0	47.0	49.0	51.0	53.0	66.5	85.0	100+	72	78	80	81	81	89	89	100+

* Straight-run reference fuel, 43.6 octane number

† Samples submitted by C. R. Wagner, Pure Oil Company, Chicago

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above,—namely, unitary, multiple coil, and catalytic,—are given in table 55. Similar data for commercial benzene are included. These results are shown graphically in figure 15. It will be noted that a straight-run gasoline of 43.6 octane number (reference fuel A-3) was used for the comparative blending tests.

The blending characteristics of UOP catalytic polymer gasoline are illustrated more completely in figure 16, in which "regular" low-sulfur polymer gasoline (see table 55 for inspection data) is blended with straight-run and cracked gasolines from various crudes. It will be noted that the
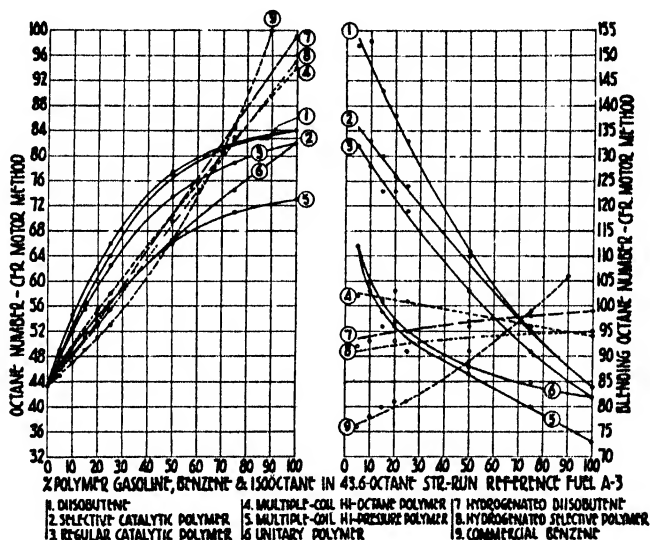

Fig. 15. Comparison of octane blending values of products produced by three polymerization methods.

blending value is lower in cracked than in straight-run gasolines. The reason is obvious.

D. Isoöctanes

In the production of isoöctane gasoline by the selective catalytic polymerization method, it may be found more economical to produce isoöctanes of 90 to 95 octane number than those approaching 100 octane. This is due, in part, to the much higher yields obtained for the lower octane products and to the good lead susceptibility of the various isoöctanes. For example, from a given quantity of gas containing both normal butene and isobutene, it is possible to produce considerably more 90–95 isoöctane than 99–100 isoöctane. The lead susceptibilities are such that the 90 and
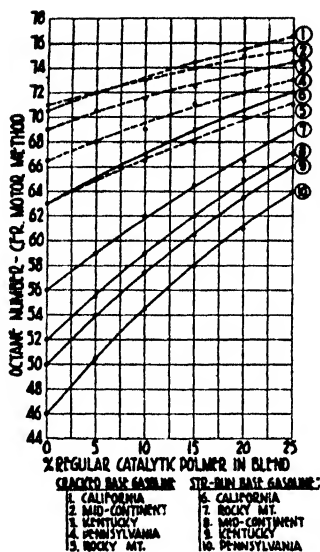
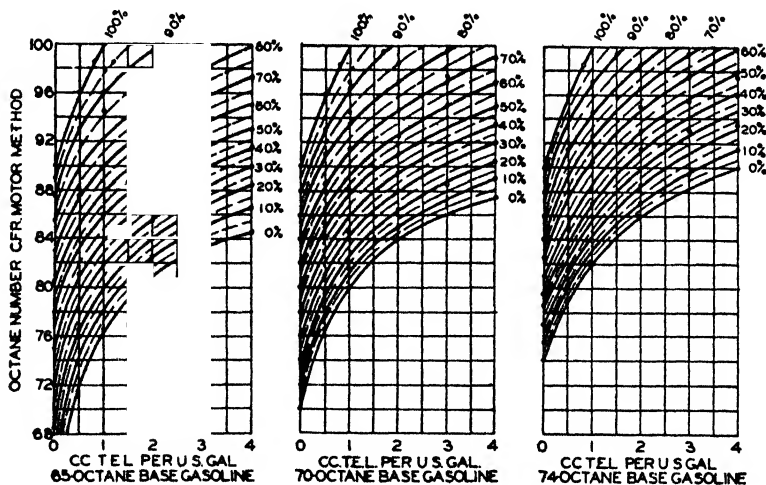FIG 16. UOP catalytic polymer gasoline blended with straight-run and cracked gasolines from various crudes.

FIG. 17. 90-octane isoöctane blended with 70-octane straight-run gasoline, with and without addition of tetraethyl lead.

95 isoöctanes can be increased to 100 octane (determined by the motor method) by the addition of 1.0 and 0.4 cc. of tetraethyl lead per U. S. gallon, respectively.

This difference in antiknock rating is due entirely to the varying proportions of different isomers which are present in the various isoöctane
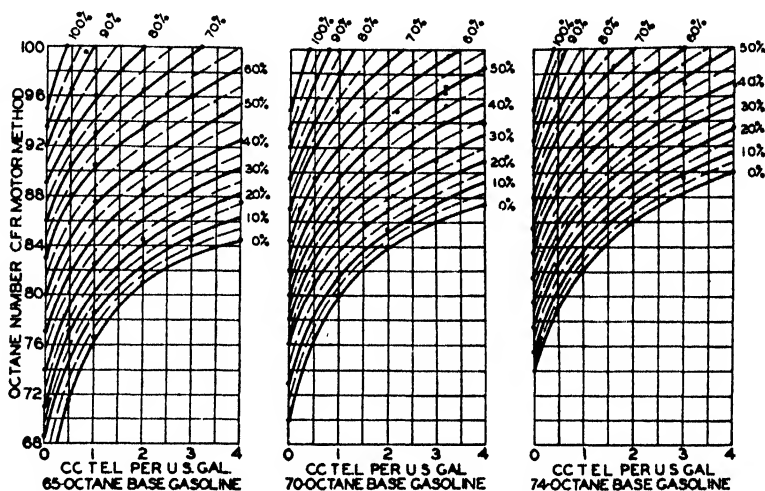

FIG. 18. 95-octane isoöctane blended with 70-octane straight-run gasoline, with and without addition of tetraethyl lead.
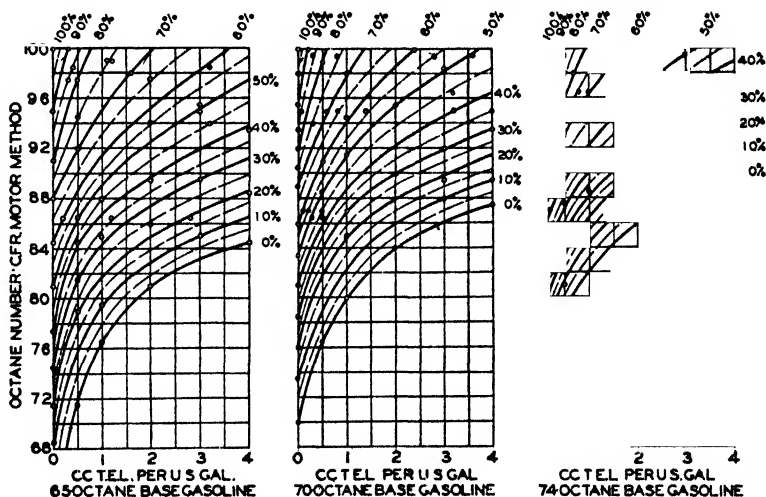

FIG 19. 100-octane isoöctane blended with 70-octane straight-run gasoline, with and without addition of tetraethyl lead.

products. For example, the isoöctane used as a standard in knock testing consists exclusively of one isomer, 2,2,4-trimethylpentane, and by defini-

tion rates 100 octane number.   The 90 and 95 isoöctanes have lower octane ratings because they consist of mixtures of different isooctanes (isomers), some of which have a lower octane rating than 2,2,4-trimethylpentane.

During the past few years isooctane has become the principal blending agent in the manufacture of high-octane aircraft fuels.   This is due to its ability to "stand up" best under the most divergent engine operating conditions, its high heat value, and its high stability without the use of inhibitors.

An interesting set of data is illustrated in figures 17, 18, and 19, in which commercial isoöctanes of 90, 95, and 100 octane rating are shown blended with 65-, 70-, and 74-octane straight-run gasolines, with and without the addition of tetraethyl lead.

E. Alcohols, ethers, and ketones from cracked gases

1. General

With the demand for motor fuels of higher octane number increasing, a number of liquids have been developed for motor fuels.   These alcohol, ether, and ketone fuels are produced from hydrocarbon gases, and their octane ratings are of the order of 100 and higher.   Generally speaking, the alcohols, ethers, and ketones are lower in fuel efficiency, owing to the lowered heat content of the oxygenated fuel, and while the octane rating is high the general efficiency is considerably lower than that of hydrocarbon fuels on a weight basis.

2. Alcohols

Ethyl alcohol is prepared from cracked gases by synthesis, although fermentation of agricultural products is the main source.

In commercial practice tertiary alcohols are generally manufactured by absorbing cracked petroleum gases which contain isobutene and other isoölefins.   Sulfuric acid of 76 per cent concentration is used as the absorbing agent.   Dilution with water hydrolyzes the mixture and the final step is steam distillation.

Further discussion of alcohols as motor fuel is given in section VII.

3. Ethers and ketones

Contrary to the behavior of ethyl ether, which is a violent knock inducer, some ethers, notably isopropyl ether, have high antiknock value and in general good susceptibility to tetraethyl lead.

Isopropyl ether is produced by chemical treatment of propene, which is present in refinery cracking plant gases or which may be produced by dehydrogenating or cracking the propane contained in both natural and refinery gases.   It is estimated that there is now sufficient propene avail-

able in the United States, exclusive of all normal demands for other purposes, to produce approximately 340 million gallons of technical

TABLE 56

Octane blending value and tetraethyl lead susceptibility of isopropyl ether

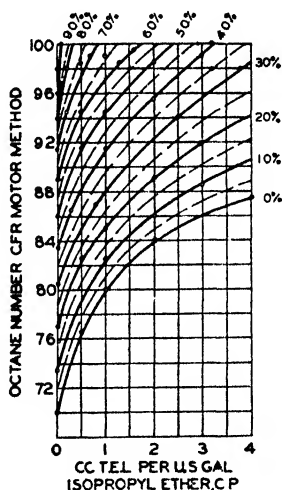| ISOPROPYL ETHER	OCTANE NO.
C.F.R. motor method:	
Straight ..	98.0
Blended 50 per cent with 70-octane straight-run gasoline*	85 5
+ 1 cc. TEL per gallon .	93 0
+ 2 cc. TEL per gallon . .	96 0
+ 3 cc. TEL per gallon	98.0
+ 4 cc. TEL per gallon . .	99 0
Army method:	
Straight. .	98.0
Blended 50 per cent with 70-octane straight-run gasoline*	87.5
+ 1 cc. TEL per gallon.	94.0
+ 2 cc. TEL per gallon ..	97.0
+ 3 cc. TEL per gallon	98 5
+ 4 cc. TEL per gallon	100.0

* California straight-run gasoline.

FIG. 20. Isopropyl ether blended with 70-octane straight-run gasoline, with and without addition of tetraethyl lead.

isopropyl ether per year. This quantity of isopropyl ether, when blended 40 per cent with gasoline and "leaded" with 3 cc. of tetraethyl lead per gallon, will equal 850 million gallons yearly of 100-octane gasoline (13, 42).

The volume of antiknock ethers could be greatly increased if mixed ethers, such as methyl isopropyl or methyl isobutyl ether, are produced.   In addition, if all the propane available in the United States were dehydrogenated to propene and converted to isopropyl ether, the potential volume of 100-octane gasoline would be increased still further.

The use of isopropyl ether as a blending agent in the production of aircraft fuels of high octane number has been described in the literature (13, 42). Its value as a blending agent is illustrated in table 56 and figure 20, in which octane ratings are given for various blends of chemically pure isopropyl ether with a 70-octane straight-run gasoline, with and without the addition of tetraethyl lead (46).   In figure 20 the straight-run base gasoline

TABLE 57

Octane ratings of blends of isopropyl ether and isooctane in straight-run gasoline (13)

PER CENT IN BLEND			OCTANE NO BY ARMY METHOD		BLENDING VALUE OF ISOPROPYL ETHER
Straight-run	Isopropyl ether	Isooctane	Clear	With 3 cc of TEL per U S gallon	
100	0	0	74 8	93 0	
70	30	0	85 7	98 4	111
70	0	30	82 0	97 0	99
70	15	15	84 1	97 6	106
60	40	0	88 3	Equals isooctane + 0.18 cc TEL per gallon	109
60	0	40	84 4	98 7	99
60	20	20	86 7	99 2	105
50	50	0	90 6	Equals isooctane + 0 44 cc. TEL per gallon	106
50	0	50	86 5	+ 0 05 cc. TEL per gallon	98
50	25	25	88.8	+ 0 08 cc. TEL per gallon	103

was a blend of reference fuels C-9 and A-4, whereas the base gasoline in table 56 was a California straight-run product.

Isopropyl ether might be used as a supplement to isooctane fuel, the ether supplying the necessary front-end volatility which isooctane lacks. Antiknock data for blends of the two products are given in table 57. Comparative data on physical properties are shown in table 58.

The octane ratings and physical properties of a number of mixed ethers (42) are given in table 59.

Ketones have also been found to have high antiknock value and good susceptibility to tetraethyl lead.   The two discussed here are acetone and methyl ethyl ketone.

Acetone may be prepared catalytically from ethanol or by special fermentation of corn or molasses.   In the latter case, both acetone and *n*-butyl alcohol are formed.   Acetone is also being produced commercially,

TABLE 58

Physical properties of C.P. isopropyl ether and isoöctane (2,2,4-trimethylpentane) (15)

PROPERTIES	ISOPROPYL ETHER	ISOÖCTANE
Boiling point, °F	153–158	211
Density at 68°F	0 725	0 691
Refractive index at 68°F	1.3680	1.3921
Freezing point, °F	−125	−162
Viscosity, centipoise at 68°F	0.322	0.543
Latent heat of vaporization, B t.u per pound	123	130
Heat of combustion:		
High value, B t u. per pound	16,900	20,580
Low value, B.t u. per pound	15,600	19,200
Low value of heat of combustion, plus latent heat of vaporization, B t u. per gallon	95,100	111,400
Reid vapor pressure, lb. per square inch at 100°F	5 3	2.2

TABLE 59

Physical properties, octane blending values, and tetraethyl lead susceptibilities of various branched-chain and mixed ethers (42)

ETHER	BOILING POINT		GRAVITY AT 60°F.		OCTANE (C.F.R. MOTOR METHOD) BLENDING VALUES,* 25 PER CENT BLEND IN 74-OCTANE AVIATION GASOLINE	
	°C.	°F.	Specific	°A.P.I.	Non-leaded	With 1 cc. of tetraethyl lead per gallon
Diisopropyl ("isopropyl")	68 4	155.1	0.722	64 5	101	105
Methyl isopropyl	31 5	88.7	0.735†	61.0	73	90
Methyl *tert*-butyl	55 3	131 5	0.735	61 0	111	106
Methyl *tert*-amyl	86 0	186 8	0 754†	56 2	108	108
Ethyl isopropyl	54 0	129 2	0 720	65 0	75	87
Ethyl *sec*-butyl	81 3	178.3	0.738	60 2	63	73
Ethyl *tert*-butyl	72 3	162 1	0 736	60 7	115	114
Ethyl *tert*-amyl	101 5	214.7	0.759†	54 9	112	106
Isopropyl *tert*-butyl	87 6	189.7	0 736	60.7	112	118
n-Propyl *tert*-butyl	98 0	208.4	0.747	57 9	103	106
Di-*sec*-butyl	114 0	237.2	0 756†	55 7	95	
Sec-butyl *tert*-butyl	114.0	237.2			106	105
Tert-butyl *n*-butyl	123 0	253.4	0.758	55.2	81	92
Tert-butyl *n*-amyl	143.0	289.4	0.770	52 3	63	80

   * Calculated blending value.

   † Other reference sources.

starting with the propene present in cracked gases. Methyl ethyl ketone is manufactured by catalytic dehydrogenation of butanol-2, which may be obtained from the butenes contained in cracked gases (77).

Octane ratings and physical properties of these ketones are given in table 60.

TABLE 60

Octane ratings and physical properties of several ketones

PROPERTIES AND OCTANE RATINGS	ACETONE	METHYL ETHYL KETONE
Boiling point:		
°C	56 1	79 6
°F	133.0	175 3
Gravity at 60°F.:		
Specific	0.795	0 808
°A.P I	46.6	43.6
Refractive index at 68°F	1 359	1 379
Freezing point:		
°C	−94 3	−86 4
°F	−137 7	−123.5
Latent heat of vaporization, B t u per pound	237.4	190 7
Heat of combustion:		
Low value, B t u per pound	12,179	13,464
High value, B.t.u. per pound	13,163	14,519
Low value of heat of combustion plus latent heat of vaporization, B t.u. per gallon	82,196	91,889
Octane No.:		
C.F.R motor method:		
Straight	100.0	98 5
Blended 50 per cent with 70-octane straight-run gasoline:*	84 5	86.5
+ 1 cc TEL per gallon	92.5	93.0
+ 2 cc. TEL per gallon	95.5	95.0
+ 3 cc. TEL per gallon	97.5	96.0
+ 4 cc. TEL per gallon	98.5	96 5
Army method:		
Straight	100.0	99 0
Blended 50 per cent with 70-octane straight-run gasoline:*	86 5	86.5
+ 1 cc TEL per gallon	94 5	93.5
+ 2 cc. TEL per gallon	98 0	96.5
+ 3 cc. TEL per gallon	100.0	98.0
+ 4 cc TEL per gallon	100.0+	99.0

* California straight-run gasoline

V. MOTOR FUEL FROM COAL

A. General

Coal as a source of motor fuel is available in any quantity desired. It is estimated that the earth contains over 7,400 billion tons of coal, which can

be converted into 1,850 billion tons of gasoline by hydrogenation. The coal can be converted into motor fuel by carbonization and hydrogenation. The carbonization process produces hydrocarbon gases, benzene, toluene, and xylenes, which are used as motor fuel. Coal is also being converted into liquid fuel by the hydrogenation process. Water gas produced from coal is being converted catalytically into gasoline. Coal or coke briquets are converted into gaseous fuels directly connected with automotive trucks and busses.

B. Benzene and other aromatics

For many years aromatic hydrocarbons, particularly benzene, have been added to motor fuels to improve their antiknock qualities. The volume of benzene used for this purpose in the United States during 1936 was 106,554,000 gallons or 0.5 per cent of the total gasoline produced (73).

Benzene is used also as a blending agent for aircraft fuel. However, owing to its relatively high freezing point (42°F.), usually less than 20 per cent may be used. Toluene, the xylenes, and ethylbenzene have lower freezing points than benzene and consequently offer greater possibilities as suitable blending agents for aircraft fuels. Toluene appears to offer the best possibilities, but has been discounted because of its high cost and its potential use as war material. It may be prepared in large quantities from coal, petroleum oils, and refinery and natural gases[2] (62).

Benzene, toluene, and xylenes are produced primarily from the high-temperature carbonization of coal and the cracking of gas oil to produce illuminating gas. The products derived from these processes are gases, liquids, and solids. The gas either is scrubbed with oil, such as creosote or gas oil, or is contacted with activated carbon to recover the benzene, toluene, and xylenes present, while the tar is distilled for its light-oil content. The impurities present in the light oil, such as free sulfur, hydrogen sulfide, carbon disulfide, thiophene, phenols, and nitrogen bases, are removed before the oil is used as motor fuel. The "crude benzol" fraction is treated with caustic soda and sulfuric acid and then distilled to the desired product.

It must be recognized that benzene, toluene, and xylenes are not used as motor fuel in the pure state, but as mixtures with olefins, paraffins, and naphthenes. Lichte (54) reports a "benzole" product as having a boiling range of 78°–165°C. (172°–329°F.) and containing 71.8 per cent of aromatic hydrocarbons, 15.5 per cent of unsaturates, 6.6 per cent of naphthenes, and 6.6 per cent of paraffins.

An American specification for "benzol" motor fuel is as follows: initial boiling point, 76°–82°C. (169°–180°F.); less than 60 per cent distilled

TABLE 61

Octane ratings and physical properties of various pure aromatic hydrocarbons

PROPERTIES	BENZENE	TOLUENE	XYLENES			ETHYL-BENZENE
			Ortho	Meta	Para	
Boiling point (81):						
°C	80 2	110 8	144 2	139 3	138 4	136 2
°F	176 4	231 4	291 6	282 7	281.1	277 1
Gravity at 60°F (81):						
Specific	0 884	0 872	0 880	0 868	0 865	0 871
°A.P.I	28.5	30 8	29.3	31 5	32 1	31 0
Refractive index at 60°F (81)	1 5044	1 4999	1 5071	1.4956	1 4986	1 496
Freezing point (81):						
°C	5 5	−95 0	−25 0	−47 4	13 4	−94 9
°F	41 9	−139 0	−13 0	−53 3	57 1	−138 8
Latent heat of vaporization, B t u per pound	166 5	155 9		149 2		146.0
Heat of combustion:						
Low value, B t.u. per pound	17,428	17,480		17,599		18,497
High value, B.t.u. per pound	18,160	18,307		18,497		18,497
Low value heat of combustion plus latent heat of vaporization, B t u per gallon	128,967	127,684		129,739		128,474
Octane No.:						
C F.R motor method:						
Straight	100+ (Isooctane + 0 5 cc TEL per gallon)	100+ (Isooctane + 0 2 cc TEL per gallon)		100+ (Isooctane + 0 2 cc TEL per gallon)		96 0
Blended 50 per cent with 70-octane straight-run gasoline:*						
Straight	80 0	81 5		84 0		85 5
+ 1 cc TEL per gallon	85.0	87 0		88 0		89 5
+ 2 cc TEL per gallon	87.5	90 0		90 5		92 0
+ 3 cc TEL per gallon	89 0	92 0		92 0		93 0
+ 4 cc TEL per gallon	89 5	93 5		93 5		94.0

	88.0	100+ (Isooctane + 0 5 cc. TEL per gallon)	100+ (Isooctane + 2 8 cc. TEL per gallon)	96.0
Army method:				
Straight	88.0			96.0
Blended 50 per cent with 70-octane straight-run gasoline:*	80 5	83 5	85 5	85 5
+ 1 cc. TEL per gallon	85 5	90 0	91 5	90.0
+ 2 cc. TEL per gallon	88 0	93 0	94 0	92.5
+ 3 cc. TEL per gallon	89 5	95 0	96 0	94.0
+ 4 cc. TEL per gallon	90 0	96 0	97 5	95 0

* California straight-run gasoline

at 100°C. (212°F.); less than 90 per cent distilled at 120°C. (248°F.); end point, 170°C. (338°F.).

The octane ratings and properties of pure benzene, toluene, xylene (ortho, meta, para), and ethylbenzene are given in table 61. Figure 21 shows these hydrocarbons blended with a 70-octane straight-run gasoline,
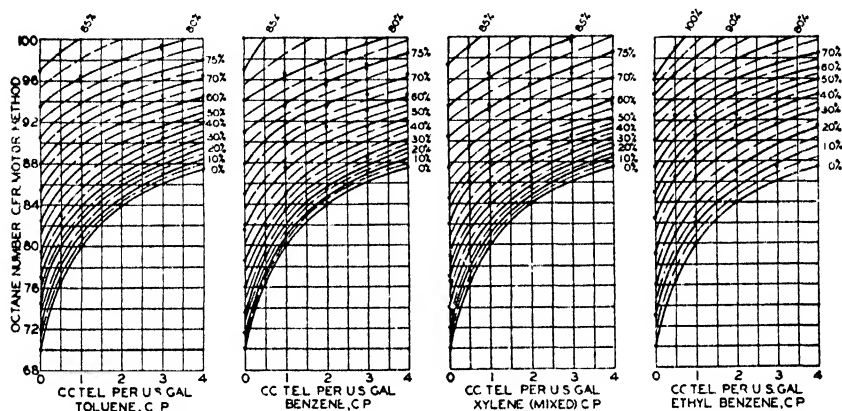

FIG. 21 Benzene, toluene, xylene, and ethylbenzene blended with 70-octane straight-run gasoline and tetraethyl lead

TABLE 62

Octane ratings of several aromatic hydrocarbons (46)

HYDROCARBONS	OCTANE NO. BY C.F.R. MOTOR METHOD BLENDED WITH 70-OCTANE STRAIGHT-RUN GASOLINE* PLUS TEL PER GALLON			
	Straight	0 cc.	1 cc.	3 cc.
o-Xylene	100+	79	82	84
m-Xylene	100+	83	89	92
p-Xylene	100+	83	89	92
Isopropylbenzene		87		98
n-Butylbenzene		82		91
tert-Butylbenzene		88		97
sec-Butylbenzene		78		90

* Blend of reference fuels C-9 and A-4.

with and without the addition of tetraethyl lead. The blending value of benzene as compared with UOP catalytic polymer gasoline, when blended in various proportions with a 44-octane straight-run gasoline, has already been illustrated in figure 15.

Antiknock data for a number of other aromatic hydrocarbons are given in table 62.

C. Hydrogenation

The hydrogenation of coal, oil, and carbon monoxide to produce motor fuel is in commercial operation in, or is projected for, Germany, England, France, Italy, Japan, and Australia.   In the United States two hydrogenation units are in operation using oil, primarily to produce oil products other than gasoline.   It is estimated that a total of about 2,775,000 tons of oil will be produced yearly when all the operating hydrogenation units and

TABLE 63

Hydrogenation units in various parts of the world (65)

COUNTRY AND PLANT	RAW MATERIALS USED	THOUSAND TONS OIL PER YEAR
Germany:		
Luena .	Brown coal	350–400
Bohlen-Magdeburg	Brown coal tar	300
Scholven	Bituminous coal	150
Plants not specified	Carbon monoxide (water gas from coke)	750
Great Britain:		
Billingham	Bituminous coal	112
Italy:		
Bari ..	Heavy oils	120-150
Livorno, Leghorn	Raw materials not given	120-150
Florence	Raw materials not given	120
France:		
Société des Produits Chimiques Courierres	Carbon monoxide	25
Japan: ˌ		
South Manchurian Railway	Coal	20
Chosen Coal Industry Co	Coal	50
Several plants	Carbon monoxide (water gas from coke)	80
United States:		4000–6000 barrels per day capacity
Baton Rouge, Louisiana .	Petroleum oils	600
Bayway, New Jersey.	Petroleum oils	600

those under design and construction are completed (65).   A list of hydrogenation units is given in table 63.

1. Coal

In the hydrogenation of coal (38), the yield of motor fuel is about 60 per cent by weight, with octane ratings ranging from 71 to 73; additional properties of the fuel are given in table 64.

In the hydrogenation of coal to motor fuel the first beneficial stage is to

clean the coal of mineral matter, which is accomplished as shown in figure 22, by floating the raw coal upon a suspension of sand and water (38, 40).

It has been found that injection of hydrogen chloride or hydrogen chloride-forming compounds during the hydrogenation of coal improves the reaction itself and the operating results by neutralizing the residual coal ash. Although hydrogen chloride is highly corrosive, this factor is overcome by pumping in an alkaline paste.
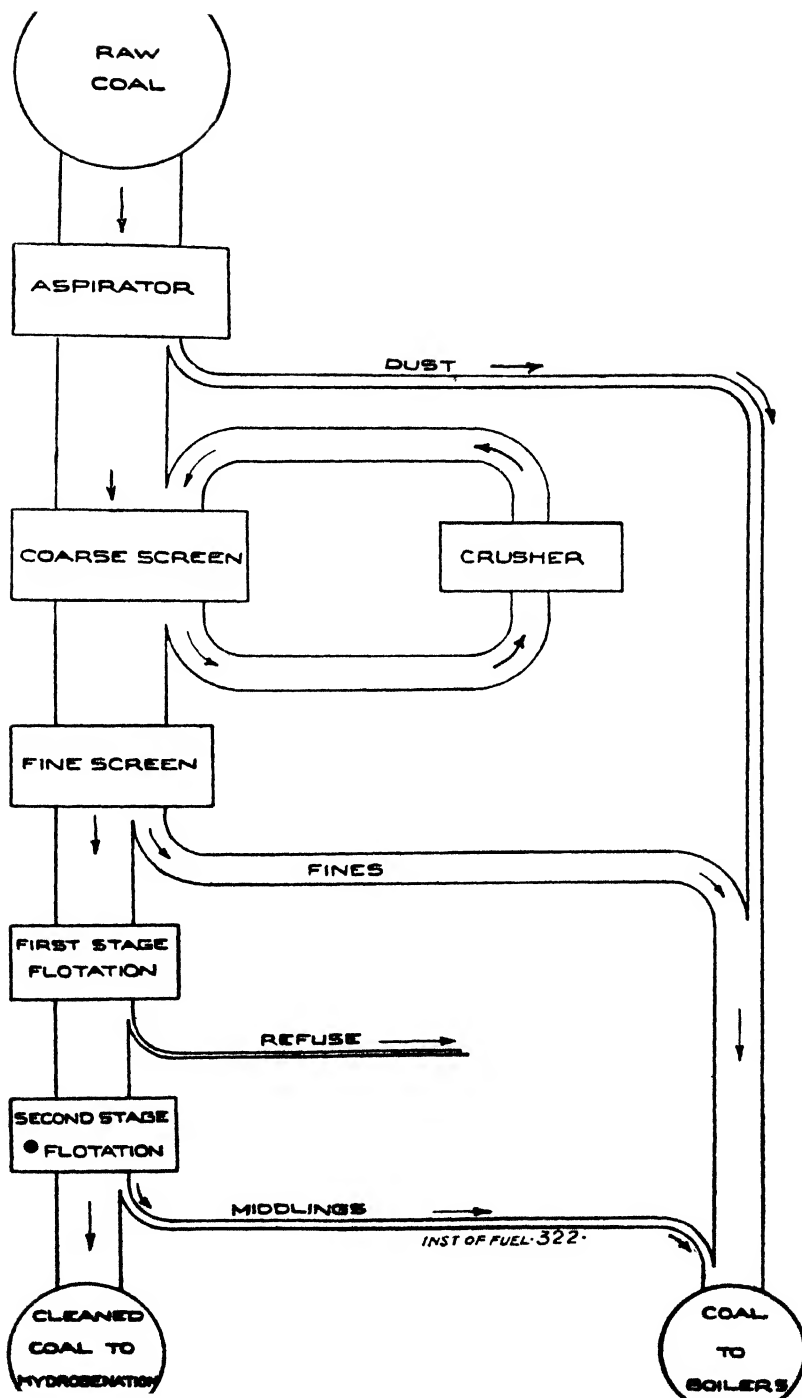
The hydrogen used in the commercial unit at Billingham, England, is produced from coke and steam and hydrocarbon gases produced from the

TABLE 64

Properties of hydrogenated motor fuel from coal (38)

Gravity at 60°F.:		
Specific		0.740-0.745
°A.P.I		59 5-58 6
Distillation characteristics:	°C.	°F.
Initial boiling point	35	95
20 per cent	70	158
40 per cent	100	212
75 per cent	140	284
90 per cent	158	316
End point	170	338
Residue, per cent	1 0	
Loss, per cent	1 0	
Reid vapor pressure, lb. per square inch at 100°F	9	
Octane No., C.F.R. motor method	71-73	
Color, °Saybolt	+25	
Odor	Marketable	
Sulfur, per cent	0 05	
Doctor test	Negative	
Corrosion	Non-corrosive	
Gum, Pyrex dish without air jet, mg per 100 cc	2 0	

hydrogenation process. A flow chart of this stage of operation is shown in figure 23.

In the flow diagrams shown in figures 24 and 25, the process of hydrogenation may be applied to coal and oil mixtures, low- and high-temperature coal-tar mixtures, or to heavy oils from low- and high-temperature carbonization of coal, for the production of motor fuel. When coal is used, it is first mixed with heavy oils to form a paste which is pumped into the apparatus. Oil is produced when coal is in contact with hydrogen gas, at a pressure of about 250 atm. and a temperature of 450°C. (842°F.), in the presence of organic tin catalysts. The hydrogenation process takes place in three stages. The first stage hydrogenates the coal paste, producing
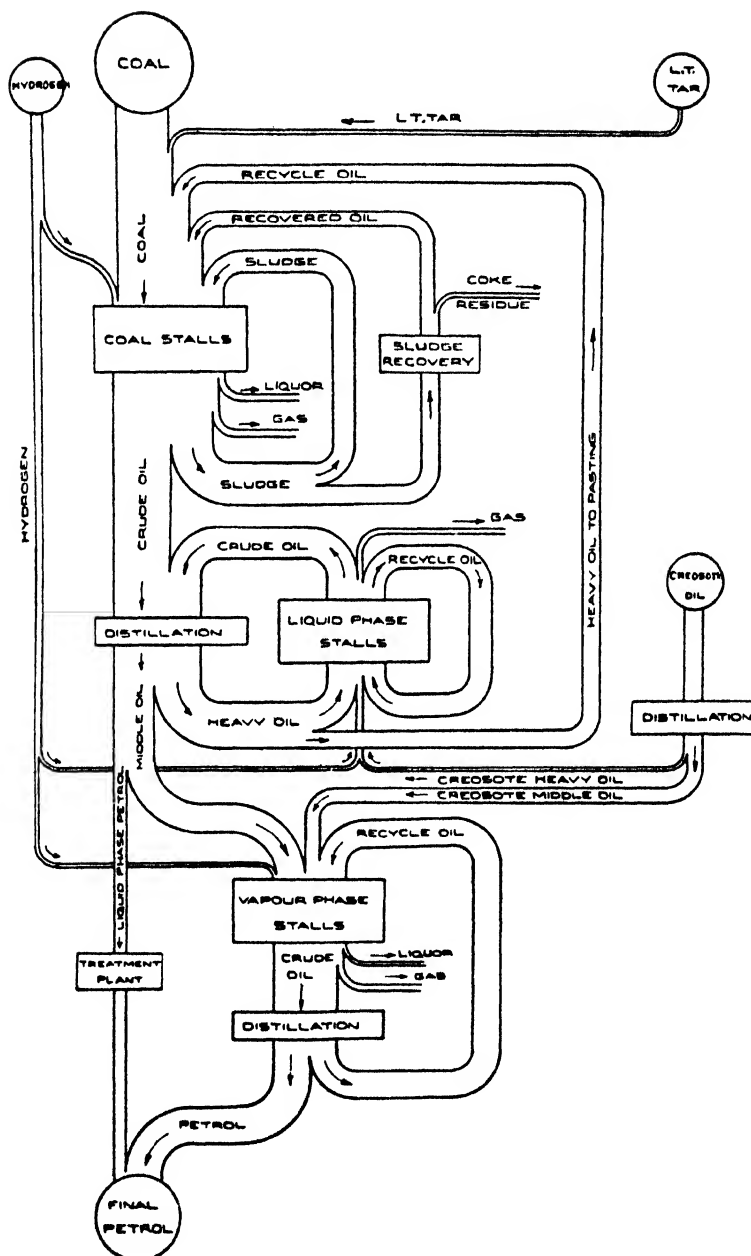
RAW COAL

ASPIRATOR

DUST →

COARSE SCREEN

CRUSHER

FINE SCREEN

FINES

FIRST STAGE FLOTATION

REFUSE →

SECOND STAGE ● FLOTATION

MIDDLINGS →

INST OF FUEL·322·

CLEANED COAL TO HYDROGENATION

COAL TO BOILERS

FIG. 23. Flow diagram of hydrogen production and treatment of hydrogenation plant gases

FIG. 24. Flow diagram for hydrogenation of coal

Fig. 25. Flow diagram of Billingham plant for hydrogenation of coal, creosote oil, and low-temperature tar.

an oil, which is fractionated into motor fuel and middle and heavy oils. The heavy oil is hydrogenated in the liquid phase to motor fuel, while the middle oil is hydrogenated in the vapor phase to gasoline. The motor fuel produced is then refined to a finished product of 71 to 73 octane number. In this process, four tons of coal are required to produce one ton of gasoline.

The Billingham coal-oil hydrogenation plant (38) to produce 150,000 tons or 1,070,000 barrels of gasoline a year cost 5,500,000 pounds or about $27,000,000 It is stated that this is substantially more than would be required for an entirely new plant of similar output (38). Nearly 4000 tons of coal per day, as shown below, are required to operate this plant:

	Tons of coal per year
Coal consumption for the manufacture of 100,000 tons per year of gasoline from coal and 50,000 tons a year of gasoline from creosote oil and low-temperature tar (including coal actually hydrogenated together with all that is used for hydrogen manufacture and power production)	600,000
For purposes other than the manufacture of gasoline	750,000
Total	1,350,000

The ratio of four tons of coal to one ton of gasoline produced can be maintained in a new plant (even if coal is used without creosote or low-temperature tar), owing to the improved methods of hydrogen manufacture which would be employed (38).

When petroleum oils are hydrogenated, the principles involved are similar to those of the coal–oil mixture operation   The two oil hydrogenation units in operation in the United States are not used primarily to produce motor fuel, but to produce special oils such as solvents and lubricants.

An interesting comparison of the results obtained by cracking and by hydrogenation are shown in tables 65 and 66.

2. Carbon monoxide from coal or coke

The Fischer–Tropsch process for converting water gas into hydrocarbon oil, called Kogasin (named from *kohle* + *gas* + *benzine*), is in commercial use in Germany and France.

This process utilizes a mixture of hydrogen and carbon monoxide with cobalt, iron, or nickel as catalysts (without alkali) at a temperature of 200°C. (392°F.) and atmospheric pressure (30).   In the presence of strong alkali the polymerization continues until solid paraffins rather than liquids are produced (32).   The theoretical yield of liquid hydrocarbons (31) is 185 g. per cubic meter of gas containing 29.5 per cent carbon monoxide and 60 per cent hydrogen.   A conversion of this water-gas mixture into

TABLE 65

Comparison of gasolines obtained by cracking and hydrogenation (40)

Hydrogenation results given are typical of low-temperature operations

Feed stock:	NAPHTHA BOTTOMS	MID-CONTINENT GAS OIL
Gravity, °A P I	30.8	33.4
Aniline point, °F	110	156
50 per cent distillation point, °F	447	540
Hydrogen content, per cent	12 0	13.8

	NAPHTHA BOTTOMS		MID-CONTINENT GAS OIL	
Products:	CRACKING	HYDRO-GENATION	CRACKING	HYDRO-GENATION
Gasoline yield, per cent	41 0	109 5	57 0	108.5
Tar yield, per cent	49 5	None	29 5	None
Gasoline octane No.*	78 5	64.0	69.6	54.0

' Series 30 engine; research method.

TABLE 66

Comparison of gasolines obtained by cracking and hydrogenation (40)

Feed stock:	WEST TEXAS CYCLE GAS OIL
Gravity, °A P I	30 3
Distillation characteristics:	
Initial boiling point, °F	400
Per cent at 460°F	56.0
End point, °F	612
Sulfur, per cent	0.192
Aniline point, °F	102

	CRACKING	HYDROGENATION			
Products:					
Gasoline yield, per cent	40 2	94 5	89 6	94 8	92 0
Gravity, °A.P I	51.0	39 8	38 6	47 8	58 4
Distillation characteristics:					
Initial boiling point, °F	104	110	98	98	96
Per cent at 212°F	25 0	13 5	16 0	25 0	33.5
Per cent at 284°F	46.0	25 0	28 5	42 0	72 0
Per cent at 356°F				45.0	67.0
Per cent at 374°F		76 0	50 5	53 0	76.0
Per cent at 400°F		88 0	70.5	71.0	
End point, °F	436	436	436	403	330
Octane No.*	79 0	82 2	85 0	82	76
Gas formation, per cent	13 0	19.0	20.4	18 8	19.5
Sulfur, per cent		0.005	0.005	0.006	0.022
For formation, per cent	21 9	0.0	0 0	0.0	0.0
Cycle gas oil, per cent	24.9	0.0	0.0	0.0	0.0

* Series 30 engine; research method.

81.6 per cent of hydrocarbons may be obtained from a two-stage operation at 184°–190°C. (363°–374°F.) using a cobalt–copper–thorium–kieselguhr catalyst. Water gas, containing 42 per cent carbon monoxide and 48 per cent hydrogen, gave a yield of 160 cc. of oil per cubic meter of water gas, using a nickel–manganese–aluminum oxide catalyst (1). On the basis of 40 lb. of coke required to produce 1000 cu. ft. of water gas (4), this is equivalent to 56 U. S. gallons of liquid hydrocarbons per short ton of coke.

Kogasin is principally a mixture of straight-chain or slightly branched-chain saturated and unsaturated hydrocarbons (51) containing: gasoline, 30°–220°C. (86°–428°F.); Diesel oil, 220°–350°C. (428°–662°F.); and wax. The gasoline fraction is water-white and sulfur-free. Fatty acids are present in small quantities (52) and olefins to over 50 per cent (72).

The nature of the hydrocarbons in Kogasin depends upon the catalyst and water-gas mixture used, cobalt producing more unsaturated oils than nickel (29). The olefin content of Kogasin from various sources is as follows:

SOURCE OF GASES	OLEFINS IN KOGASIN GASOLINE PER CENT BY VOLUME	
	Nickel catalyst	Cobalt catalyst
Water gas ($CO.H_2 = 1:1$)	35	55
Mixed gas ($CO:H_2 = 1:2$)	16	35
Cracked gas ($CO:H_2 = 1:3$)	5	12

The water gas used for catalytic conversion to hydrocarbons is derived commercially from the reaction of steam upon coke or gases such as methane. A relatively high degree of purity of water gas is required, owing to the poisoning effect upon the catalyst of hydrogen sulfide and organic sulfur compounds. A water gas derived from coke and steam, having the composition of 6 per cent carbon dioxide, 40 per cent carbon monoxide, 50 per cent hydrogen, and 4 per cent nitrogen, methane, and oxygen, was reported by Martin as a commercial gas for catalytic conversion to hydrocarbons (57).

The flow chart of the process is shown in figure 26, where the water gas from coke and steam passes to a gas holder and then to purifiers to remove hydrogen sulfide, carbon disulfide, mercaptans, etc. The purified water gas passes on to the catalytic reaction chamber where conversion to gaseous, liquid, and solid hydrocarbons takes place at a temperature of about 190°C. (374°F.) and atmospheric pressure. The reaction is exothermic and heat must be abstracted. The heat of reaction is 600 cal. per cubic meter of water gas. The control of the temperature may be carried out according to Studien and Verwertungs (69) by circulating water,

steam, or oil under pressure through a nest of tubes surrounded by the catalyst bed. The hydrocarbon products leaving the catalytic chamber pass into a tower counterflow to a stream of cooling water. The liquefied hydrocarbons and water are separated in a tank. The hydrocarbon gases from the water cooling system are absorbed in activated carbon, steam distilled, and the gasoline recovered. The propane and butane produced are condensed to liquids. The Kogasin oil is then passed to a pipe still
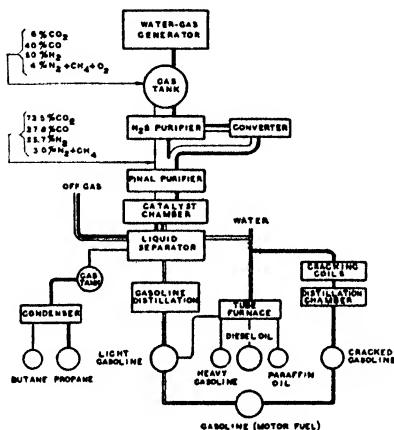

FIG. 26. Flow diagram of catalytic water-gas reaction

TABLE 67

Primary products of catalytic water-gas reaction (57)

PRODUCTS	YIELD	OLEFINS PRESENT
	per cent	per cent
Propane, propene, butane, and butene.	8	50–55
Gasoline distilling to 392°F	60	30–35
Gas oil	22	5–6
Paraffin wax, melting point, 68°–212°F	10	

and fractionating unit, where it is separated into gasoline, kerosene, Diesel oil, and paraffin oil. The gasoline recovered from the activated carbon passes to a distillation unit to be separated into a light and heavy fraction.

The Kogasin oil or fractions thereof may be pumped to a cracking unit where it is converted to motor fuel of high octane rating and blended with the gasoline produced from the distillation of the primary oil.

The process of converting water gas catalytically into hydrocarbons at atmospheric pressure yields primary products (57) such as given in table 67.

TABLE 68

Properties of gasolines produced by the catalytic water-gas reaction (57)

Light primary products:

BOILING POINT OF FRACTIONS	OCTANE NO	GRAVITY AT 60°F	
		Specific	°A.P.I.
°F			
262	66	0.670	79.7
270	64	0.670	79 7
284	62	0.673	78 7
297	58	0 675	78.1

Gasoline produced:

BOILING RANGE OF RAW MATERIALS	BOILING RANGE OF GASOLINE PRODUCED	OCTANE NO	GRAVITY AT 60°F.	
			Specific	°A.P.I
°F.	°F.			
297·662	Up to 383	65–70	0 730	62 3
132·662	Up to 383	65–70	0 725	63.7

TABLE 69

Yields and quality of light gasoline fractions from Kogasın oil

Yields, volume per cent of Kogasin oil:										
Gasoline ..		20 0		33 8		43 5		56.3		68 4
Bottoms ..		79.8		66 0		56.0		43 5		31.4
Recovery.		99 8		99.8		99 7		99.8		99.8
Loss		0 2		0.2		0.3		0 2		0 2
Properties of light gasolines:										
Gravity at 60°F.:										
°A.P.I.		84 1		79 3		75.8		72.4		69.6
Specific		0 6563		0 6713		0 6826		0 6940		0.7036
Octane No., C.F.R. motor method		73		66		58		49		40
	°F.	°C	°F.	°C.	°F.	°C.	°F.	°C.	°F.	°C.
Distillation characteristics:										
Initial boiling point	84	29	104	40	110	43	97	36	107	42
10 per cent	108	42	124	51	138	59	140	60	155	68
20 per cent..	114	46	134	57	150	66	160	71	176	80
50 per cent	129	54	162	72	190	88	214	101	247	119
90 per cent	172	78	210	99	252	122	298	148	359	182
End point	209	98	250	121	299	148	350	177	396	202
Per cent over		96.5		98.0		98.0		98 0		98.0
Per cent bottoms		1.0		1.5		1 0		1.5		1 0
Per cent loss		2.5		0 5		1 0		0 5		1.0

The gasolines of varying boiling ranges have the properties (57) shown in table 68.

TABLE 70

Properties of Kogasin oil

Gravity at 60°F.:		
°A.P.I.		63.0
Specific		0.7275
Sulfur, per cent ..		0 01
Octane No , C F R. motor method .		20
	°F.	°C.
100-cc. Engler distillation:		
Initial boiling point	113	45
5 per cent ..	148	64
10 per cent	170	77
20 per cent	205	96
30 per cent . .	245	118
40 per cent .. .	286	141
50 per cent . .	323	162
60 per cent	368	187
70 per cent ..	420	216
80 per cent .	487	253
90 per cent	657	347
End point ..	702	372
Per cent over .		97.5
Per cent bottoms . . .		1.0
Per cent loss		1 5

TABLE 71

Properties of gas oil from Kogasın

PROPERTIES	GAS OIL	DIESEL OIL MIXTURE
Color		Brown
Specific gravity, d²⁰°	0 835–0.91	0 866
Cold test, °C .	0°	
Viscosity (Engler)	2 6	1.28
Flash point	65°	68°
Boiling point	Lowest 60 per cent at 300°C.	320° (End)
Alkali-soluble .	4 per cent	2 per cent
Water-soluble	0 5 per cent	0
Cetane No. .	Over 100	56

The data relating to gasolines (28) from Kogasin oil and their properties are shown in table 69.

A distillate analysis of the Kogasin as produced is shown in table 70.

Diesel oils are also produced from the hydrogenation of carbon monoxide by the Fischer–Tropsch process. It is reported (73) that a gas oil derived from Kogasin oil has a cetane number of over 100. The data concerning this gas oil and a mixture with a low cetane number are shown in table 71.

The motor fuel derivable from Kogasin by means of distilling a light fraction therefrom, reforming the naphtha cut, cracking the residue (bottoms), and catalytically polymerizing the olefins present in the cracked gases and blending the four fractions, will yield 84.3 per cent of a 66-octane product. The results (28) are shown in table 72.

TABLE 72

Products produced from Kogasin oil (28)

YIELD OF PRODUCTS FROM KOGASIN OIL	PER CENT BY VOLUME
Light gasoline	29.1
Reformed gasoline from naphtha	26 8
Cracked gasoline from bottoms .	22 6
Polymer gasoline	5 8
Total gasoline .. .	84 3
Octane No. of blends of all gasolines .	66

3. Gas from coal carbonization

Hydrocarbon gas produced by the carbonization of coal in coke ovens is used not only for household and industrial heating, but also as motor fuel in trucks and busses in Germany.

There are now over forty filling stations (68) in Germany where city gas (methane–ethane) is available in high-pressure holders, at pressures up to 5000 lb., for recharging containers on trucks and busses just as gasoline tanks are filled at ordinary gasoline stations. Special types of containers have been developed for this use. Weights and dimensions of two sizes to withstand approximately 3000 lb. pressure most generally used are as follows:

CAPACITY	DIAMETER	LENGTH	WEIGHT
gallons	*inches*		*lb.*
14.0	9	5 ft. 0 25 in.	138
20.9	13	5 ft. 8 in.	300

A schematic drawing of a typical truck installation is shown in figure 27. In this case, the cost of converting a medium-sized truck to operate on city gas is stated to be from $40 to $60.

4. Gasified coal and coke directly in motor vehicle

There are two types of gas-driven motors used in Germany at the present time (39). The simplest type is that using the compressed city gas (methane–ethane) in high-pressure holders. The second type is that which carries its own gas generator as an integral part of the motor vehicle. The use of this gas generator is less expensive than the liquid fuels produced in the country and its continued use is expected, since wood, brown coal, coal, and coke are native fuels.

Coal or coke is used for producing fuel gases for motors the principle of which is Diesel operation. With a few alterations the Diesel engine may be converted into a high-compression gas-burning machine which is suitable because of heavy construction. Gas conduits and carburetors on the modern installations, as well as improved mixing equipment, have
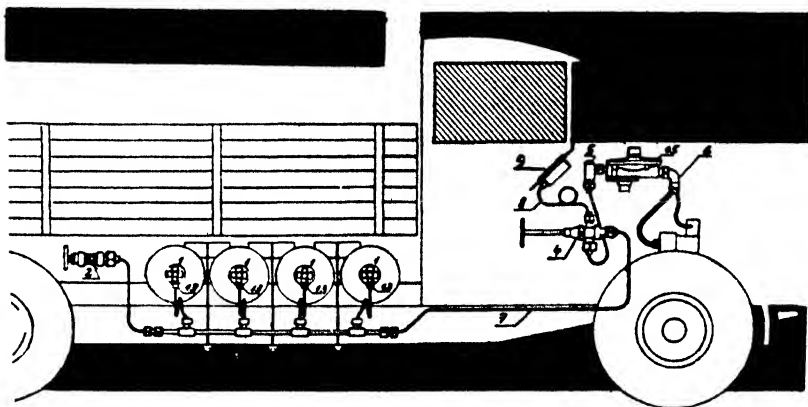
FIG. 27. Schematic drawing of typical truck installation for burning methane–ethane gas mixture

raised the power economy. Some of the problems necessary to work out in connection with these motors have been the removal of dust from the gas generator and an adequate gas-cooling system which removes as much water as possible from the gas before it passes to the combustion chamber. These problems have been met by the use of centrifuges and filters. A flow diagram of the mechanism is shown in figure 28.

The fuels used in the gas generator have presented difficulties in operation, owing to the types of fuels themselves which are available for use. Peat and brown coal must be coked, owing to their high water content. These fuels have been used in France, England, and Belgium. Peat coke was found to be an especially suitable fuel, owing to its hardness, high energy content and low ash, with very little sulfur present. It is nearly like charcoal in its characteristics and may be used in charcoal generators.
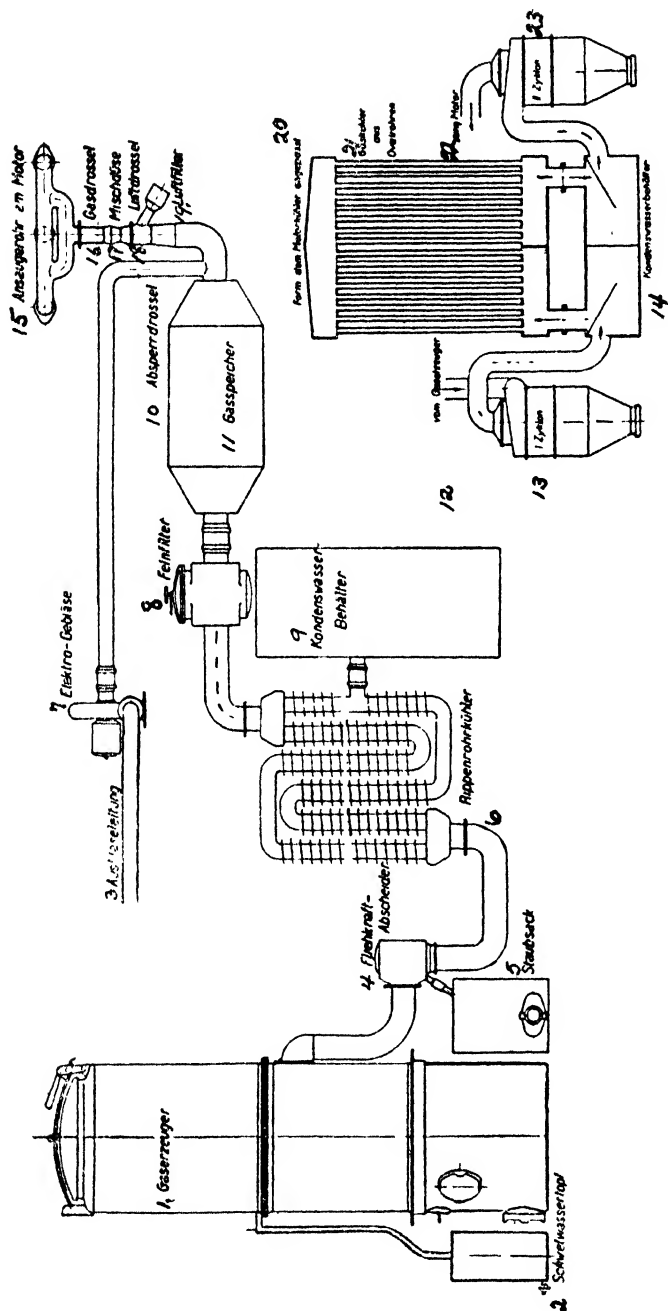
FIG. 28. Flow diagram of a Diesel engine converted into a high-compression gas-burning machine

1. Gas generator
2. Cold-water tank
3. Exhaust pipe
4. Centrifugal separator
5. Dust filter
6 Radiator cooler
7. Electric bellows
8. Fine filter
9. Condensed-water tank
10. Cut-off throttle
11. Gas accumulator
12. From gas generator
13 Cyclone separator I
14. Condensed-water tank
15. Suction tube from motor
16 Gas throttle
17. Mixing nozzle
18. Air throttle
19. Air filter
20 Form of motor cooler, fitted oval tube
21. Gas cooler
22 To motor
23 Cyclone separator II

The limitations found in using coal for gaseous motor fuel are due to its low reactivity. As a comparison, the gasification temperatures of each of the solid fuels are given:

Charcoal	900°–1000°C.
Brown coal	1100°–1200°C.
Coal	Above 1400°C.

The tendency in France, Belgium, and England has been to raise the temperature in the firebox as high as possible. In Germany, lower temperatures and gas velocities have been used and the resulting poorer gas quality is improved by adding steam.

The particular field of gas-producing vehicles has been heavy trucking, but they are not limited to that field alone. Italy has required all omnibusses to be operated on generator or compressor gases by the end of 1936; this type of installation has also been used in small river boats on the Rhine. Possibilities of producer gas automobiles have also been studied.

VI. MOTOR FUEL FROM OIL SHALE

The oil shale resources of the world are enormous. The shales vary widely in their oil content from a few gallons per ton to over one hundred. Commercial plants to produce oil from shale are in operation in Scotland, France, Esthonia, and Manchuria. The oil shales are subjected to high-temperature treatment in retorts. The vapors evolved are condensed and refined to marketable products such as gasoline, kerosene, gas oil, heavy oils, and waxes.

The heavy oils, which may or may not contain the kerosene and gas-oil fractions, have been cracked into gasoline. Typical oils derived from shales of France, Manchuria, Australia, Esthonia, Spain, South Africa, and Sweden were subjected to high temperatures and pressure in order to convert them into high-octane gasoline. The yield of gasoline ranged from 38 to 65 per cent, depending upon the quality of the charging stock and mode of operation. The yields, quality of products, and operating conditions are shown in table 73.

VII. MOTOR FUEL FROM PLANTS AND WOOD

A. Alcohol

1. Fermentation process

Alcohol, chiefly ethyl and methyl, is used in many countries for blending with gasoline as motor fuel. Ethyl alcohol is used in greater volume than methyl. Both may be prepared by synthesis. However, most of the

TABLE 73

Shale oils

Source of charging stock	Manchurian Shale Oil		Australian Shale Oil			Estonia		Spain Blended Cracking Stock		South Africa			Swedish Shale Oils			French Shale Oil	
			Bunker C	Pitch						Torbanite	Shale oil	2 parts Torbanite and 1 part shale oil					
Charging stock analysis:																	
Gravity, °A.P.I	26.6		26.2			18.2		21.7		26.0	21.6	24.6	14.6			25.4	
Engler distillation.																	
Initial boiling point, °F	430		308			104		384		212	225	202	230			292	
10 per cent	508		415			293		448		322	339	325	339			389	
20 per cent	556		502			306		485		410	410	400	413			456	
50 per cent	669		660			548		570		613	607	606	625			610	
90 per cent	756		758			746		734			743					738	
End point	760+							744								760	
Per cent at 400°F	0.0		8.5			24.0		1.0		19.0	18.5	20.0	41.0			11.5	
Per cent at 572°F	24.5		30.0			47.0		24.0		43.0	43.0	44.5				43.0	
Sulfur, per cent by weight	0.60		0.59			0.63		0.5				0.65	1.81			0.60	
B. B. & W., per cent	2.0 Wax		Trace			0.4		0.3					0.1				
Cold test, °F	95		16 at 77°F.			Below zero					356° End point	392° End point	Below zero			55	
Viscosity (S.F.) sec. at 122°F	10					15		14					15 at 77°F			13 at 77°F	
	Resid-uum	Non-residuum						Resid-uum	Coke		Gasoline	Gasoline				Resid-uum	Coking
Throughput and yields:																	
Per cent of charge:																	
Gasoline	38.2	64.8	44.2	52.2	47.5	43.7	37.5	41.4	60.0		47.8	43.8	42.8	42.1	41.8	49.3	69.1
Residuum	56.0	0.0	37.9	34.8	34.5	49.9	60.1	45.5			47.3	55.5	55.2	51.0	45.9	45.6	None
Coke	5.8	35.2	1.2						95.3		4.4	0.7					
Gas and loss			17.9	13.0	18.0	6.4	2.4						2.0	6.9	12.3	5.1	30.9
Barrels per day on stream:																	
Coke, lb. per barrel of charging stock.	84.0																
Gas, cu. ft. per barrel of charge	290	697	605	655	613	290	176	544	932		304	134	196	269	399	374	638

Analysis of products:

	59.2	57.9	63.9	62.5	61.9	52.7	53.0	60.0	60.2	58.7	53.3	46.4	45.9	46.9	55.2	56.1
Gasoline:																
Gravity, °A.P.I.	59.2	57.9	63.9	62.5	61.9	52.7	53.0	60.0	60.2	58.7	53.3	46.4	45.9	46.9	55.2	56.1
A.S.T.M. distillation:																
Initial boiling point, °F	95	96	99	90	98	102	103	98	105	108	108	106	110	108	94	99
10 per cent	143	147	136	135	137	165	171	148	147	162	182	218	215	201	157	163
20 per cent	178	184	162	166	167	198	205	178	171	198	219	252	258	245	201	205
50 per cent	270	270	220	230	231	270	270	240	236	257	290	307	307	299	294	292
90 per cent	362	377	320	328	326	361	352	330	330	321	372	364	366	362	368	367
End point, °F	391	393	368	377	370	393	389	388	388	355	393	402	403	392	391	381
Octane No., A.S.T.M., motor method	61	60	75	75	74	73	73	67	66	63	61	89	89	90	66	67
Octane No., research method	64	63	68					74	74	71	63				72	72
Gum, copper dish, mg. per 100 cc.	452	604			47	1163	503			205	192	276	182	256	217	844
Residuum:																
Gravity, °A.P.I	13.7		5.4	2.1	0.3	0.5	4.2	6.4		6.9	9.7	2.4	-0.1	-2.7	7.1	
Viscosity, (S.F) sec at 122°F	32		242	842	1984	274	78	112		62	37	95	197	2400+	40	
B.S. & W., per cent	2.0 Wax		0.6	0.6	1.2	0.4	0.4	3.9		5.2	3.0	0.1	0.2	0.3	0.2	
Sediment by extraction, per cent	0.33															
Flash, Cleveland open cup, °F	270		290		280	210	225	250		260	240	235	200	220	280	
Flash, Pensky–Martens, °F	170		150		180	190	205	182		210	205	195	190	200	185	
Cold test, °F	85		40		70	+65	30	60		50	40	25	60	70	15	
Operating conditions:																
Heater outlet, temperature, °F	925					920	910			875	875					
Light-oil heater outlet, temperature, °F			900(A) Furnace									900	900	900		
Heavy-oil heater outlet, temperature, °F					950(B) Furnace							900	900	900		
Reaction chamber, pressure, lb. per square inch	250		200			350	348			200	200	200	200	200		

ethyl alcohol is derived from the fermentation of agricultural products such as beet sugar, molasses, potatoes, and corn.

TABLE 74

Alcohol consumed as motor fuel in foreign countries (27, 71) for the year 1934

COUNTRY	METRIC TONS CONSUMED
Austria	4,400
Czechoslovakia	42,477
France	293,600
Germany	180,000
Hungary	8,731
Italy	5,000
Jugoslavia	6,592
Latvia	6,457
Poland	5,941
Spain	12,000
Sweden	12,250
Total	577,448

TABLE 75

Octane blending value of ethyl alcohol (27, 61)

FUEL	OCTANE NO , C F.R. MOTOR METHOD		
	Of blend	Increase due to alcohol	Blending value of alcohol
Gasoline No 1:			
Straight	63 0		
5 per cent alcohol	67 5	4 5	152
10 per cent alcohol	72 0	9 0	153
15 per cent alcohol	76 5	13 5	153
Gasoline No. 2:			
Straight	61 0		
5 per cent alcohol	66.4	5 4	168
10 per cent alcohol	70 4	9 4	155
15 per cent alcohol	75 0	14.0	154

In the United States during 1936 the production of ethyl alcohol amounted to about 100 million gallons, of which 10 per cent was produced from cracked gases.

The volumes of alcohol consumed in eleven foreign countries (27, 71) for the year 1934 are shown in table 74.

The advantages of ethyl and methyl alcohol when compared to most gasolines are high octane rating and blending value and high latent heat of

vaporization. The octane blending value of alcohol depends upon the percentage of alcohol in the blend and upon the octane rating and chemical composition of the base fuel. Typical data (27, 61) are given in table 75.

The high latent heat of vaporization of alcohol is particularly valuable in reducing manifold temperature. This permits a greater weight of charge to be taken into the cylinders, thereby increasing the power output of the engine.

TABLE 76

Physical properties of various alcohols

PROPERTIES	ALCOHOLS							
	Methyl	Ethyl	Butyl	sec-Butyl	Isobutyl	tert-Butyl	n-Amyl	tert-Amyl
Boiling point:								
°C	64 5	78.5	117.7	99.5	107.3	82 8	137.9	101.8
°F	148 1	173 3	243 9	211 1	225 1	181.0	280.2	215.2
Gravity at 60°F :								
Specific	0 795	0 792	0 813	0.811	0 805	0 792	0 820	0.812
°A P.I	46.4	47 1	42 5	43.0	44.3	47 1	41.1	42.7
Refractive index at 68°F	1 329	1 361	1 399	1 397	1 396	1 387	1 414	1.406
Freezing point:								
°F	−144.0	−179.1	−129 6	−128 2	−162.4	+77 9	−109 3	10.6
°C	−97 8	−117 3	−89 8	−89 0	−108 0	+25 5	−78.5	−11.9
Latent heat of vaporization, B t u per pound	511 7	367 7	254 3	241 9	248 5	234.8	216.3	190.5
Heat of combustion:								
Low value, B t u per pound	8,352	11,523	14,269	14,269	14,269	14,037	14,969	14,775
High value, B t.u per pound	9,542	12,765	15,555	15,555	15,555	15,323	16,267	16,073
Low value of heat of combustion plus latent heat of vaporization, B t u per gallon	58,678	78,260	98,323	97,948	97,268	94,194	103,716	101,167

Even with these advantages, ethyl and methyl alcohol show a marked decrease in efficiency as measured by fuel consumption. This is due to the relatively low heating value of these low molecular weight alcohols (27, 55). Compared to gasoline as 100 per cent (21,140 B.t.u. per pound, gross heating value), the values of methyl and ethyl alcohol are 45 and 66 per cent, respectively. The heating values of the higher alcohols are somewhat higher; tertiary butyl and tertiary amyl alcohols are about 73 and

76 per cent, respectively, with normal butyl and amyl alcohols at 74 and 77 per cent, respectively. Thus the tertiary alcohols, or alcohols containing at least four carbon atoms, have a heat value approximately 75 per cent that of gasoline (see table 76).

In addition to the heating value advantage of the tertiary alcohols, they have greater susceptibility to tetraethyl lead than the lower alcohols (67), as indicated in tables 77 and 78.

It will be noted that, although a number of alcohols effect an appreciable increase in octane number, their tetraethyl lead susceptibilities vary over a wide range. The tertiary butyl and tertiary amyl alcohols show a lead susceptibility equal to or better than that of the straight-run base fuel.

TABLE 77

Octane blending values and tetraethyl lead susceptibilities of various alcohols (67)

FUEL	OCTANE NO *		OCTANE NO. INCREASE DUE TO	
	Nonleaded	With 1 cc. of TEL per gallon	Alcohol	Tetraethyl lead†
Straight-run base gasoline	68 2	77 7		9 5
30 per cent alcohol in base gasoline:				
Ethyl	77 5	82 1	9 3	4 6
Butyl .	69.9	71 0	1.7	1.1
sec-Butyl .	76 0	79 8	7 8	3 8
Isobutyl	75 2	77.1	7 0	1 9
tert-Butyl .	77.5	87 2	9 3	9 7
n-Amyl	66 0	68 8	2.2	2 8
tert-Amyl ..	75 2	86 6	7.0	11 4

* Determined on series 30 engine at 900 R.P.M and 375°F. jacket temperature. This is substantially equivalent to the C.F R. motor method.

† Tetraethyl lead susceptibility, i.e., increase in octane rating due to the addition of 1 cc. of TEL per gallon

Road and laboratory tests conducted with a 10 per cent ethyl alcohol-gasoline blend have indicated a fuel consumption at least 4 per cent higher than with gasoline alone. The results of "official" road tests (27, 63) conducted by the American Automobile Association, the National Bureau of Standards, the National Automobile Chamber of Commerce, the American Petroleum Institute, and others are shown in table 79.

C.F.R. dynamometer tests (27) with gasoline and a 10 per cent alcohol-gasoline blend of equal octane rating gave results as shown in table 80.

Aside from this increased fuel consumption with alcohol–gasoline blends, the use of alcohol introduces certain operating difficulties such as starting, acceleration, and vapor lock (27, 12). The lower or water-soluble alcohols

TABLE 78

OCTANE NOS. OF FUELS CONTAINING VARIOUS ALCOHOLS

FUEL	Methyl†	Ethyl†	n-Butyl	Isobutyl	sec-Butyl	tert-Butyl	Amyl	tert-Amyl
C.F.R. motor method:								
Straight	98 0	99 5	87 5	87.5		100+ (isoöctane + 3 cc. TEL per gallon)	77.5	100+ (isoöctane + 0.2 cc. TEL per gallon)
Blended 50 per cent with 70-octane								
straight-run gasoline	89 0	88.5	81 5	82 0	85 0	83.5	72 5	84.5
+ 1 cc. TEL per gallon	91 5	89.0	84 5	84 5	87 0	91.0	79.0	89.5
+ 2 cc. TEL per gallon	93.5	89.0	86 5	86 0	88.5	95.0	82.0	92.0
+ 3 cc. TEL per gallon	95 0	89.5	87 5	87 0	89.0	97.0	83.5	92 5
+ 4 cc. TEL per gallon	96 0	89.5	88 5	87 0	89 5	99.5	84.5	93.0
Army method:								
Straight						100+ (isoöctane + 3 cc. TEL per gallon)		100+ (isoöctane + 0.5 cc. TEL per gallon)
Blended 50 per cent with 70-octane								
straight-run gasoline*	85 5	86.5	80 5	84.5		85.5	72.5	85.0
+ 1 cc. TEL per gallon	87.5	87.0	83 5	86 0		93.0	78 0	91.0
+ 2 cc. TEL per gallon	88.0	87 0	85.0	87.5		97.0	80.5	93.5
+ 3 cc. TEL per gallon	88.0	87.5	85.5	88.5		99 0	82.5	94.0
+ 4 cc. TEL per gallon	88 0	87.5	85 5	89.0		100.0+	84 0	

* California straight-run gasoline.

† Blend contained 40 per cent of methyl and 10 per cent of ethyl alcohol.

are difficult to blend with gasoline unless they are substantially anhydrous or unless a binder such as benzene, toluene, or one of the higher alcohols (*n*-propyl, isopropyl, *n*-butyl, isobutyl, or *tert*-butyl) is used.

Alcohol blends can also cause considerable corrosion and solvent troubles with certain materials commonly used in the construction of motor car and aircraft engines, such as aluminum alloys used in fuel tanks, carburetor float-bowl castings, etc.

As to the future use of alcohol-gasoline blends as aircraft fuel, opinions differ. According to F. R. Banks (7): "Alcohol fuels have not justified

TABLE 79

Increase in fuel consumption over gasoline when using a 10 per cent alcohol-gasoline blend (27, 63)

MAKE OF CAR	PER CENT INCREASE IN FUEL CONSUMPTION WITH A 10 PER CENT ALCOHOL-GASOLINE BLEND	
	By weight	By volume
1933 Chrysler "6" sedan	4 87	4.13
1933 Oldsmobile "6" sedan	3 81	3.07
1932 Ford "V-8" coupe	10 20	9.51
1932 Rockne "8" convertible sedan	3 75	3 06
Average	5 66	4.94

TABLE 80

Comparative C.F.R. dynamometer tests with 10 per cent alcohol-gasoline blend and gasoline alone (27)

FUEL	BRAKE HORSEPOWER	POUNDS OF FUEL PER BRAKE HORSE-POWER HOUR	PER CENT INCREASE IN CONSUMPTION
Gasoline	2 19	0 75	
10 per cent alcohol-gasoline blend	2 19	0.78	4.0

themselves as constituents of aviation gasoline, even in those countries where the respective governments have fully supported their use by subsidy or monopoly.

"It is a feature that they do not deteriorate in the ordinary sense of the word, but they can and do preignite violently when subjected to certain operating conditions of the engine.

"The principal advantage of the alcohols, ethyl and methyl, is that they have a high latent heat of vaporization. Even when blended with gasoline in amounts up to about 20 per cent, this feature is particularly valuable in reducing the "boost" or supercharge temperature; thus allowing a

greater charge weight to enter the cylinders of the engine, thereby improving its power output.

"Therefore, although it would be unsafe to dogmatize regarding the use of these alcohols as constituents of aviation fuel, they appear to be very critical to operating conditions, and their employment is uneconomical

"The higher alcohols, such as isopropyl, have been investigated, but do not at the moment appear to offer any particular advantage."

According to A R Ogston (64): "Certain of the higher alcohols, such as isopropyl, are likely to prove very valuable anti-detonants

"The utility of alcohol as an anti-detonant arises from both its very high spontaneous ignition temperature and its exceptionally high latent heat of vaporization; the latter property would largely overcome the difficulties which arise from the high boost temperatures created by superchargers and may even obviate the necessity for intercoolers Certain alcohols are also very efficient de-icers of the induction system (in aircraft engines)

"One of the most suitable methods of utilizing the properties of alcohol will be by supplying it to the carburetor from a separate tank installed in the aircraft, rather than use of a ready mixed blend fed from the main fuel tank The separate alcohol feed could be controlled by the pilot, and probably need be used only when the engine has to be operated in excess of say 70 per cent maximum power or during icing conditions."

B Gasified wood

Wood, as far as history advises us, was the first source of heat and power that man used The early settlers of North America over 300 years ago began using wood from the 900 million acres of forest land for their energy supplies Wood is still an important source of energy, as it represents over 7 per cent of the total which was used in the United States during the year 1934 (25) The consumption of wood for the production of energy is far greater in the rest of the world than in the United States It is interesting to note that in some countries which have relatively large sources of oil the steam locomotives are still being fired with wood In the case of Rumania this is due to the desire of the government to keep the wood choppers employed. Countries which have no oil deposits are utilizing other fuel resources to some extent, such as coal, oil shale, and wood

In Germany, Italy, and France wood or the product of its carbonization is converted into gas which is used as fuel in motor busses and trucks. Italy has several hundred such motor vehicles in operation Many motor busses or trucks propelled by the gasification of wood cannot be distinguished in outward appearance from cars using gasoline or Diesel engines Gasoline itself can be produced from the tar obtained from the distillation

of wood, the yield being about 40 gallons per ton   By cracking, 26 per
cent of motor fuel, 21 per cent of Diesel oil, and the balance fuel gas and
coke can be produced   Illustrations of the application of wood-burning
motors (39) are shown in figures 29, 30, and 31

Fig 29   The wood-gas generator set up in a motor bus
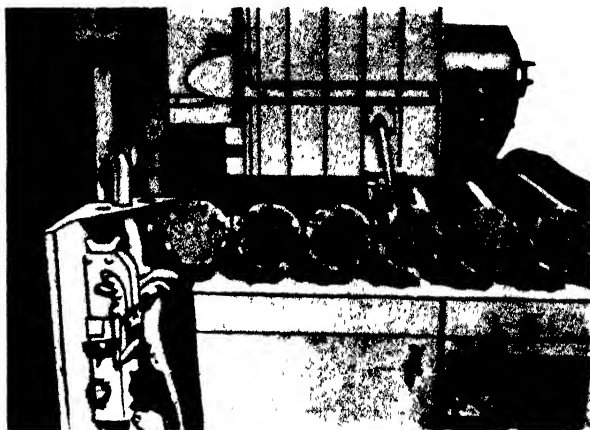
Fig 30   Gas purifiers of the wood burner with baffle plates

VIII. COMPOUNDS ADDED TO IMPROVE OCTANE AND CETANE NUMBERS OF FUELS

A. Tetraethyl lead for gasoline

An effective method for improving the antiknock quality of motor fuels
is the use of tetraethyl lead   For Q-grade and premium-grade Ethyl

gasolines, it is added in the form of "Q" Ethyl fluid; for leaded aircraft fuels, in the form of "IT" Ethyl fluid   The composition of each varies from time to time as researches prove certain mixtures more desirable. At present (21), the respective compositions are shown in table 81.

The antiknock ingredient of Ethyl fluid is tetraethyl lead   It is important, therefore, that when reference is made to the addition of Ethyl fluid
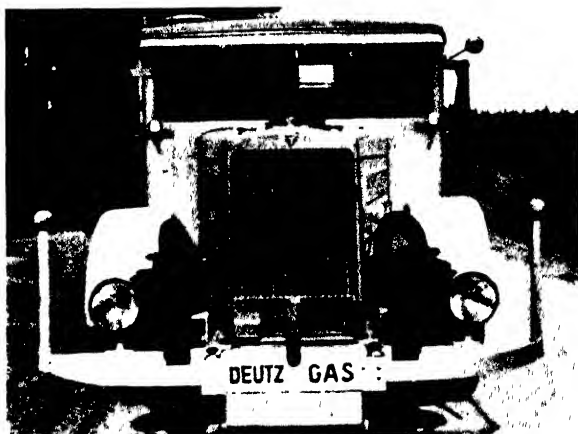
FIG 31   Wood-gas purifier on a Humboldt-Dietz motor

TABLE 81

Composition of Ethyl fluid (21)

COMPOSITION, PER CENT BY VOLUME	"Q" FLUID	"IT" FLUID
Tetraethyl lead	63 30	61 42
Ethylene dibromide	25 75	35 68
Ethylene dichloride	8 78	
Kerosene	1 10	1 75
Dye	0 13	0 25
Impurities	0 94	0 90
Total	100 00	100 00

to a gasoline, the quantity of tetraethyl lead only should be specified, as for example, 1 cc TEL per gallon

The response of a fuel to the addition of tetraethyl lead varies according to the chemical composition of the fuel and to the amount of impurities, such as free sulfur or sulfur compounds, present in the fuel   The variation in tetraethyl lead response for commercial base gasolines is illustrated in

figure 32.   The effect of chemical composition on lead response is shown
in tables 82 and 83

TABLE 82

Effect of chemical composition on tetraethyl lead susceptibility (46)

C P FUELS BLENDED 50 PER CENT WITH 70-OCTANE STRAIGHT-RUN GASOLINE*	OCTANE NO , C F R MOTOR METHOD			
	Of blend	With TEL per gallon		
		1 cc	2 cc	3 cc
Isooctane (2,2,4-trimethylpentane)	84	92	96	98
Isopropyl ether	86	94	99	100+
Isopentane	81	90	93	96
Benzene	82	88	90	92
Toluene	82	88	90	92
o-Xylene	79	82		84
m-Xylene	83	89		92
p-Xylene	83	89		92
Ethylbenzene	85	90	93	95
n-Butylbenzene	82			91
tert-Butylbenzene	88			97
sec-Butylbenzene	78			90
Isopropylbenzene	87			98
Mesitylene	85			96
Cyclohexane (not blended)	77	78	79	80
Hexane (not blended)	62	74	79	81

* Blend of reference fuels C-10 and A-4

TABLE 83

Tetraethyl lead susceptibility of solvent-extracted gasolines (extracts) (66)

BLENDS OF 63 4 OCTANE MID-CONTINENT STRAIGHT-RUN GASOLINE WITH	OCTANE NO , C F R MOTOR METHOD		
	Of blend	With TEL per gallon	
		1 cc	2 cc
25 per cent of 91-octane extract	70 0	77 0	80 1
50 per cent of 91-octane extract	77 5	81 7	83 6
50 per cent of 98-octane extract	79 0	82 8	84 7
50 per cent of 100-octane isooctane	79 7	84 9	

Interesting data on lead susceptibility for a number of gasolines from
different sources (41) are given in table 84

A number of years ago it was discovered that the tetraethyl lead sus-
ceptibility of certain distillates was substantially reduced after treatment
with acid or plumbite (41).   This is illustrated in figure 33 for a West

Texas straight-run gasoline tested under the following conditions: A, untreated; B, Doctor-treated; C, acid-treated, plant scale; D, acid-treated, laboratory scale; E, sample D, redistilled; F, sample D, neutralized before removing sludge.

It will be noted that, in all except the untreated sample (sample A), there was a lag in the action of the tetraethyl lead. This lag amounted

TABLE 84

Tetraethyl lead susceptibility of various gasolines (41)

GASOLINE	OCTANE NO. C F R. MOTOR METHOD	TEL SUSCEPTI- BILITY*
Straight-run gasolines:		
Mid-Continent	46.1	1.28
West Texas	54.1	0.77
Hendricks	59.8	0.73
Yates	58 8	0.77
Texas Panhandle (3)	60 7	0 85
Okmulgee (Okla) (3)	45.2	0 97
California	69 5	1.31
Pennsylvania (3)	50.0	0.95
Kansas (3)	44 7	0.77
Cracked gasolines:		
Okmulgee (Okla.) (3)	67.0	1 33
Mid-Continent and Texas, Doctor-treated	70 5	0.78
Kansas (3)	62 6	1 00
Texas Panhandle (3)	58.5	0 76
Natural and aviation gasolines:		
Special-cut natural, 9 7-lb Reid vapor pressure (3)	64 1	2.00
Stabilized natural	69 3	1 81
Stabilized natural, 13.0-lb. Reid vapor pressure (3)	67 2	1 46
Natural, 10.0-lb Reid vapor pressure (3)	60 5	1 38
Black Bayou-White Castle aviation	79 0	1 59
Smackover aviation	70.0	1 55
Gulf Coast aviation (3)	62 1	1 55
West Texas aviation	71 0	1 66

* See literature reference (41) for method determining the tetraethyl lead susceptibility values given in this column; the higher the numerical value, the greater the lead response.

to over 5 cc. per gallon in the case of the laboratory treated sample (D), showing "that apparently some compound had been formed in the gasoline which probably combined with the tetraethyl lead in the gasoline, rendering it inactive. However, in all cases except F, the action of the tetraethyl lead was apparently normal after a certain concentration had been reached" (41). The increase in lead susceptibility after redistillation is "not be-
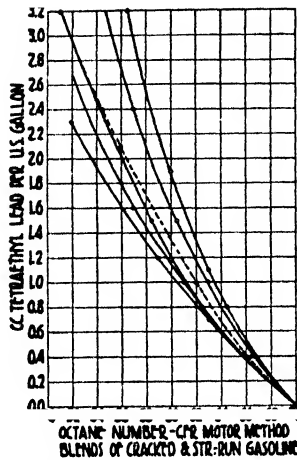
FIG. 32. Tetraethyl lead susceptibility of base stocks used for commercial gasoline
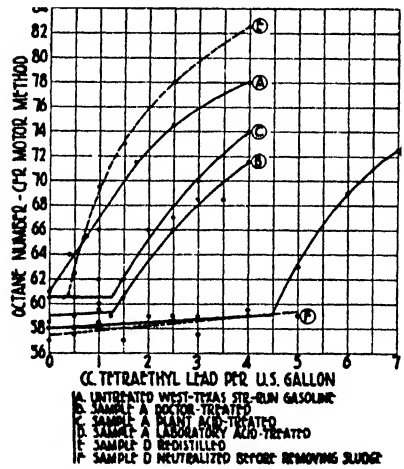
FIG. 33. Effect of treating and sweetening on tetraethyl lead susceptibility

lieved to be due to an increase in volatility, but to the removal of disulfides and other sulfur compounds" (41). In this connection, a sample of an apparently similar West Texas straight-run gasoline was doped with 0.35 per cent of dimethyl sulfate, with the following results (41):

WEST TEXAS STRAIGHT-RUN GASOLINE	OCTANE NO., C.F.R. MOTOR METHOD	TEL SUSCEPTIBILITY
Undoped	60 0	0.83
+ 0.35 per cent dimethyl sulfate	59.2	0.73

Although the gasoline doped with dimethyl sulfate did not show the above-mentioned lag in the action of the tetraethyl lead, both the octane rating and the lead susceptibility were reduced.

Other investigators (10) have also found the presence of sulfur compounds to affect tetraethyl lead susceptibility adversely, as shown in table 85.

Additional data on the effect of sulfur compounds on tetraethyl lead susceptibility are given in table 86.

Tetraethyl lead susceptibility has a distinct bearing on the refiner's problem of "reforming" versus "leading." Both methods are used to raise a low-octane straight-run gasoline to a marketable product. In

TABLE 85

Effect of sulfur compounds on tetraethyl lead susceptibility (10)

SAMPLE	OCTANE NO., C.F.R. MOTOR METHOD		
	Nonleaded	With TEL per gallon	
		1 cc.	3 cc.
Venezuelan straight-run gasoline: .	64 4	73.8	82.3
+ 0.1 per cent sulfur as EtSH .	63 6	68.7	74.3
+ 0.1 per cent sulfur as Et$_2$S	64.6	70.5	76.6
+ 0.1 per cent sulfur as Et$_2$S$_2$.	64.0	68.8	73.4
+ 0.1 per cent sulfur as Et$_2$S$_3$ . .	62.0	66 6	73 0
Iranian gasoline:	55.3	66.3	75.6
+ 0.1 per cent sulfur as EtSH	55.0	61.7	68.2
+ 0.1 per cent sulfur as Et$_2$S	55.4	62.8	69.8
+ 0.1 per cent sulfur as Et$_2$S$_2$ ..	55.4	61.5	68.2
+ 0.1 per cent sulfur as Et$_2$S$_3$ . . .	52.5	59 7	66.3
Heptane–octane: .	55.3	68.3	77.8
+ 0.1 per cent sulfur as Et$_2$S$_2$ . .	55.3	61.4	67.3

certain cases it has been found more economical to use a combination of both methods. A recent report (36) on the subject summarizes the magnitude of the differential revenue derived for optimum reforming and leading versus no reforming, as follows (using gasoline at 6 cents per gallon and fuel oil at 60 cents per barrel):

OCTANE ELEVATION	OCTANE TEST METHOD	REFORMER CHARGE BARRELS PER DAY	INCREASED REVENUE PER YEAR
70	Motor	5,000	$365,000
73	Motor	5,000	425,000
73	Research	5,000	470,000
73	L-3	5,000	515,000

B. Nitrites, nitrates, etc., for Diesel fuels

The demand for Diesel oils of high cetane number is increasing.   Highly selected stocks of paraffinic characteristics are in demand.   To increase

TABLE 86

Effect of sulfur compounds on tetraethyl lead susceptibility of reference fuels

SAMPLE	OCTANE NO., C F.R. MOTOR METHOD	
	Nonleaded	With 2 cc TEL per gallon
Reference fuel A-3	44	58
+ free sulfur	41	54
+ ethyl sulfate	43	47
+ ethyl sulfide		56
+ diethyl sulfide	42	
+ ethyl mercaptan	42	
+ butyl sulfide	43	56
+ diphenyl sulfide	44	57
+ isoamyl sulfide		56
+ diphenyl disulfide	43	53
+ isoamyl disulfide	42	
+ isoamyl mercaptan	43	53
+ thiophene	44	57
+ thiophenol		54
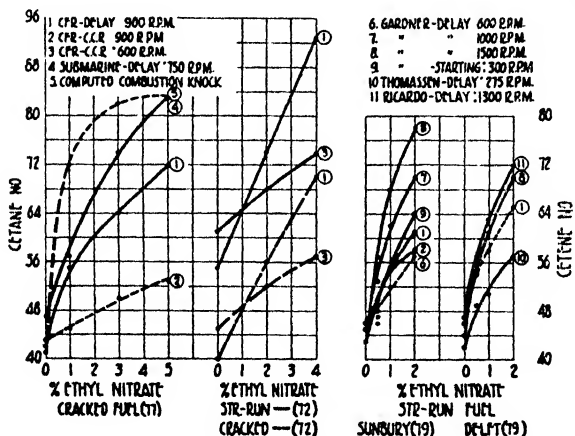
Fig. 34. Effectiveness of ethyl nitrate for improving ignition quality of Diesel fuels

the cetane number many compounds have been proposed to accomplish this purpose such as: (*1*) alkyl nitrates, e.g., ethyl, isopropyl, and butyl nitrates; (*2*) alkyl nitrites, e.g., ethyl, isopropyl, butyl, and amyl nitrites;

(*3*) nitro compounds, e.g., nitrobenzene, nitrotoluene, nitroxylol, nitroglycerol, and nitropentane; (*4*) oxidizing agents, e.g., nitrogen dioxide, percarbonates; (*5*) peroxides, e.g., cyclodiacetone, cyclotriacetone, acetyl, tetralin, tetrahydronaphthalene, and benzoyl peroxide; (*6*) aliphatic hydrocarbons, e.g., allylene, diacetylene, and butadiene; (*7*) bromine compounds, e.g., benzyl, butyl, and butylene bromides and isobutylene dibromide; (*8*) oxygenated copper compounds, e.g., copper oleate and copper stearate; (*9*) hydroxylamines, diketones, etc. Few data are to be found as to the relative values of these dopes. The effectiveness of ethyl nitrate (47, 37, 11), acetyl peroxide (11), and tetralin peroxide (60) is illustrated in figures 34 and 35.
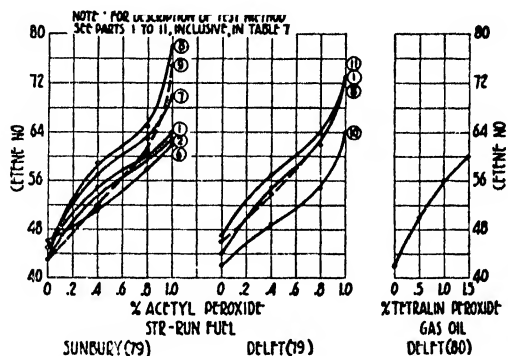
FIG. 35. Effectiveness of acetyl peroxide and tetralin peroxide for improving ignition quality of Diesel fuels

IX. 100-OCTANE AIRCRAFT FUELS

The general procedure for producing 100-octane aircraft fuels is to blend commercial isoöctane with an aviation straight-run gasoline and add up to 3.0 cc. of tetraethyl lead per gallon. In many cases, 5 to 15 per cent of isopentane is used to supply the front-end volatility which isoöctane lacks.

Toluene, benzene, ethylbenzene, isopropyl ether, mixed ethers, alcohols, ketones, and other high-octane blending agents may be used in the preparation of 100-octane aircraft fuels, provided the finished product meets specifications. The advantages and disadvantages of these various fuels have been discussed to a limited extent in the respective sections of this paper.

The high vapor pressure (20.4 lb. per square inch) of isopentane limits to less than 15 per cent the amount of isopentane that can be used and still meet the 7- and 7.5-lb. Reid vapor pressure specifications which are now in force in the United States.

Because of the high freezing point (approx. 42°F.) of benzene, usually not more than 10 per cent can be blended and still meet the conventional freezing-point specification of −76°F.

The relatively low heating value of isopropyl ether (19 per cent lower than isooctane on a weight basis) and its reaction to the acid-heat test tend to prevent its use to any great extent under existing specifications.

TABLE 87

Various combinations of high-octane blending agents and straight-run base gasolines to produce 100-octane fuel, with and without addition of tetraethyl lead

	C F.R. MOTOR METHOD PER CENT HIGH-OCTANE FUEL FOR VARIOUS ADDITIONS OF TEL PER GALLON				
	0 cc.	1 cc	2 cc.	3 cc	4 cc
(1) Per cent blended with 74-octane straight-run gasoline* (46):					
Isooctane (100 octane No.) ..	100	69	58	51	43
Isoöctane (95 octane No)	100+ 0.4 cc.	84	70	60	50
Isoöctane (90 octane No)	100	85	72	62	
(2) Per cent blended with 70-octane straight-run gasoline* (46):					
Isoöctane (100 octane No.)	100	74	63	55	48
Isoöctane (95 octane No.)	100+ 0 4 cc.	85	72	63	55
Isoöctane (90 octane No.) ..	100	88	81	72	
Isopropyl ether (98 octane No.) ..	100+ 0 1 cc.	68	56	42	34
Isopentane (90 octane No.)	100+ 0 7 cc.	88	74	62	52
Benzene (100+ octane No.) . . .	86	84	82	81	76
Toluene (100+ octane No.) .. .	87	85	83	81	77
Xylene (mixed) (100+ octane No.)....	86	84	82	80	77
Ethylbenzene (96 octane No.) .	100+ 0 7 cc.	97	88	82	76

* Blend of straight-run reference fuels C-9 and A-4.

It is apparent, therefore, that isoöctane is destined to remain one of the principal blending agents in the manufacture of high-octane aircraft fuels. This is because of its high octane rating, good susceptibility to tetraethyl lead, high heating value, good stability without the use of inhibitors, and its ability to "stand up" best under the widest variety of engine operating conditions.

The dollar value of high-octane fuel when used in the high-compression aircraft engine has been discussed quite completely in the literature (46,

7, 13, 50, 8, 19). The following statements presented by D. P. Barnard (8) illustrate the economic value of octane ratings: (1) Depending upon design and operating conditions, the revenue-earning power of 1 gallon of gasoline may be increased from 2 to 5 cents per octane number improvement. (2) If the octane number increase involves a decrease in energy content, the apparent improvement must be discounted by about two octane numbers for each per cent reduction in heat content below that of gasoline. (3) It is evident that the earning power of octane increase is so great that within practical limits its cost cannot influence the trend toward higher octane numbers to any appreciable extent.

In tables 87 and 88, data are given showing various combinations of

TABLE 88

Various combinations of high-octane blending agents, straight-run base gasolines, and tetraethyl lead to produce 100-octane fuel

| | PER CENT HIGH-OCTANE FUEL FOR VARIOUS ADDITIONS OF TEL PER GALLON | | | |
| | Motor method | | Army method | |
	2 cc.	3 cc.	2 cc.	3 cc.
1. Components (67):				
Per cent straight-run (74-octane No.).		38 37 37		
Per cent isoöctane (100-octane No.)		62 53 46		
Per cent isopentane (90-octane No.).		0 10 17		
2. Components:				
Per cent straight-run (70-octane No.)*.	25 24	32 31	26 25	35 34
Per cent isoöctane (95-octane No.)	75 66	68 59	74 65	65 56
Per cent isopentane (90-octane No.) .	0 10	0 10	0 10	0 10

* California straight-run gasoline.

fuels and tetraethyl lead which rate 100 octane number by the C.F.R. motor method. In a number of cases octane ratings by the Army method are included. Most of the data have already been presented in the respective sections of this paper.

X. SUMMARY

Motor fuels of any desired octane rating are available from many sources in ample quantities for years to come. The fuel requirements for internal-combustion engine use can be met at any time and in any quantity.

The sources of motor fuels are petroleum, natural gas, coal, oil shale, plants and wood. Compounds added to motor fuels play their part in obtaining greater efficiencies.

XI. REFERENCES

(1) AICHER, A., MYDDLETON, W. W , AND WALKER, J.: J. Soc. Chem. Ind. **54**, 313T-20T (1935).

(2) ALDEN, R. C · Am. Petroleum Inst. Bull. 10, No. 2 (II), 87 (1929).

(3) ALDEN, R. C.: Natl. Petroleum News **24**, No 3, 32 (1932).

(4) American Gas Association: Combustion, 3rd edition (1932).

(5) Anon: Petroleum World (Los Angeles) **31**, No 1, 22 (1934).

(6) Anon: Natl. Petroleum News **29**, No. 15, 19 (1937)

(7) BANKS, F. R : J. Inst Petroleum Tech. **23**, No 160, 61-177 (1937).

(8) BARNARD, D P.: Natl. Petroleum News **29**, No 13, 65-70 (1937).

(9) BIRCH, S F , PIM, F. B., AND TAIT, T.: J Soc Chem. Ind. **55**, 335-7T (1936)

(10) BIRCH, S. F , AND STANSFIELD, R.: Ind Eng Chem **28**, 668-72 (1936).

(11) BOERLAGE, G. D., BROEZE, J. J., LeMESURIER, L J , AND STANSFIELD, R : J. Inst. Petroleum Tech **22**, No 153, 455-68 (1936).

(12) BRIDGEMAN, O C : Ind Eng Chem. **28**, 1102-12 (1936).

(13) BUC, H. E , AND ALDRIN, E E : S A E Journal **39**, No 3, 333-57 (1936).

(14) BUCHANAN, D. E.: Paper presented at the Second World Petroleum Congress, Paris, France, June 14-19, 1937.

(15) BURRELL, G. A , AND TURNER, N. C : Natl. Petroleum News **26**, No. 11, 22 (1934)

(16) CHILDS, R. B.: Handbook Propane-Butane Gases. 2nd edition (Supplement), p 31 (1937).

(17) Composite Catalogue Oil Refinery and Natural-Gasoline Plant Equipment, Process Handbook Section, p. 278 (1936)

(18) COOKE, M. B., SWANSON, H R , AND WAGNER, C R : Natl. Petroleum News **27**, No. 47, 33-44 (1935)

(19) CRONSTEDT, VAL, AND DuBois, R. N : Paper presented at Annual Meeting of the Society of Automotive Engineers, Detroit, January 11-15, 1937.

(20) DUNSTAN, A. E.: J. Soc. Chem. Ind **51**, Nos. 41 and 42, 846-55 (1932)

(21) EDGAR, GRAHAM: Private communication

(22) EGLOFF, GUSTAV: Natl. Petroleum News **27**, No. 47, 25-32 (1935).

(23) EGLOFF, GUSTAV: Oil Gas J. **35**, No. 22, 58 (1936).

(24) EGLOFF, GUSTAV: Ind Eng Chem. **28**, 1461 (1936).

(25) EGLOFF, GUSTAV: Sci. Monthly **42**, 291-300 (1936).

(26) EGLOFF, GUSTAV: Natl. Petroleum News **27**, No. 47, 65-72 (1937).

(27) EGLOFF, GUSTAV, AND MORRELL, J C.: Ind. Eng Chem **28**, 1080-8 (1936)

(28) EGLOFF, GUSTAV, NELSON, E. F., AND MORRELL, J C : Ind. Eng. Chem. **29**, 557 (1937).

(29) FISCHER, F.: Brennstoff-Chem. **16**, 1-11 (1935).

(30) FISCHER, F , AND KOCH, H.: Brennstoff-Chem. **13**, 428-34 (1932).

(31) FISCHER, F., AND PICHLER, H.: Brennstoff-Chem. **17**, 24-9 (1936)

(32) FISCHER, F., AND TROPSCH, H.: Proc Intern. Conf Bituminous Coal **1926**, 238, 239, 243.

(33) FITZSIMONS, O.: U S. patent 2,063,597, December 8, 1936

(34) FRIEND, W. Z : Handbook Propane-Butane Gases, 2nd edition, pp. 175-9 (1936).

(35) GARNER, F. H., EVANS, E B., SPRAKE, C. H , AND BROOM, W E. J.: Proc. World Petroleum Congress, London, **2**, 170 (1933).

(36) GARY, W. W., AND ADAMS, N. R.: Natl. Petroleum News **29**, No. 32, R83-90 (1937).

(37) Good, R F : S A. E. Journal **40**, No. 6, 232–41 (1937).

(38) Gordon, K : J. Inst. Fuel **8**, 10–17 (1935); Génie civil, May 2, 1936.

(39) Hartner-Seberich, R : Brennstoff-Chem. **17**, 1–11 (1936).

(40) Haslam, R. T., and Russell, R. P.: Proc. Am. Petroleum Inst., 11th Annual Meeting, Section III, p. 86 (1930).

(41) Hebl, L. E., Rendel, T. B., and Garton, F. L.: Ind. Eng. Chem. **25**, 191 (1933)

(42) Hoffman, E , Lapeyrouse, M., and Sweeney, W. J : Paper presented at the Second World Petroleum Congress, Paris, France, June 14–19, 1937.

(43) Howes, D. A.: Proc. World Petroleum Congress, London, July 19–25, 1933, pp. 781–3.

(44) Hubner, W H., and Egloff, Gustav: Natl. Petroleum News **28**, No. 32, 25–30 (1936); UOP Booklet No. 189.

(45) Hubner, W. H , and Egloff, Gustav: From Cetane No. – Diesél Index No. Relationship as given in UOP Booklet No. 209, "A Study of Diesel Fuels"; paper presented at a meeting of the American Society of Mechanical Engineers, Pennsylvania State College, August 18–21, 1937.

(46) Hubner, W. H , Egloff, Gustav, and Murphy, G. B : Natl. Petroleum News **29**, No 30, R57–R71 (1937).

(47) Hubner, W. H., and Murphy, G B.: Natl Petroleum News **28**, No. 4, 22–8; No. 5, 25–8 (1936); UOP Booklet No 176.

(48) Hubner, W H., Murphy, G. B , and Egloff, Gustav: Paper presented at the Second World Petroleum Congress, Paris, France, June 14–19, 1937.

(49) Keith, P. C., and Ward, J T.: Natl. Petroleum News **27**, No. 47, 52–63, 72 (1935).

(50) Klein, F. D : S A E. Journal **39**, No 2, 304 (1936).

(51) Koch, H., and Ibing, G : Brennstoff-Chem. **16**, 185–90, 261–8 (1935).

(52) Koch, H., Pichler, H., and Kölbel, H : Brennstoff-Chem. **16**, 382–7 (1935).

(53) Krieger, G. G : Oil Gas J. **35**, No 25, 42–4 (1936).

(54) Lichte: Oel Kohle Erdoel Teer **12**, 459 (1936).

(55) Lichty, L C , and Ziurys, E U.: Ind. Eng. Chem. **28**, 1094–1101 (1936).

(56) Lovell, W G., Campbell, J. M , and Boyd, T A : S. A. E. Journal **26**, No. 2, 163 (1930); Ind. Eng. Chem. **20**, 1045 (1928); **23**, 555 (1931).

(57) Martin, F.: Oel Kohle Erdoel Teer **27**, 691–7 (1937).

(58) Minerals Year Book, p. 1055 (1937).

(59) Morrison, L. H., and Adams, O.: Diesel Power and Transportation **15**, No. 8, 557 (1937).

(60) Moser, F. R : U. S. patent 2,011,297, August 13, 1935.

(61) National Research Council, Ottawa, "Use of Grain Alcohol in Motor Fuel in Canada," p. 34, April 21, 1933.

(62) Neptune, F. B , Trimble, H. M , and Alden, R. C : Natl. Petroleum News **28**, No. 19, 25–30 (1936).

(63) Official Tests of Regular and Alcohol-Blended Motor Fuels, Joint Committee Report on Performance Characteristics of Regular and Alcohol-Blended Motor Fuels, June, 1933, pp. 5–6.

(64) Ogston, A. R.: J. Inst. Petroleum Tech. **23**, No. 166, 506 (1937).

(65) Petroleum Technology in 1936, pp. 230, 231, 252.

(66) Saegebarth, E., Broggini, A. J., and Steffen, E.: Proc. Am. Petroleum Inst., 7th Mid-Year Meeting, Section III, p. 56 (1937).

(67) Schneider, H. G.: U. S. patent 2,087,582, July 20, 1937.

(68) Smith, A. J. G.: Gas Age-Record **80**, No. 4, 28 (1937).

(69) STUDIEN AND VERWETUNGS: British patent 451,177 (1936).
(70) SULLIVAN, F. W.: U. S. patent 2,034,495, March 17, 1936.
(71) TOKAYER, O.: World Petroleum **7**, No. 6, 309–18 (1936).
(72) TROPSCH, H , AND KOCH, H : Brennstoff-Chem. **10**, 337–46 (1929).
(73) U. S. Bur. Mines Monthly Petroleum Statements
(74) U. S. Bur Mines Repts Investigations No. 3311 (September, 1936) and No. 3348 (May, 1937).
(75) VOORHEES, V.: U S. patent 2,079,887, May 11, 1937.
(76) WALTON, M. R : Private communication.
(77) WHITMORE, F. C : Organic Chemistry, pp. 250–62. D. Van Nostrand Co., New York (1937).
(78) WILSON, R E., AND BARNARD, D. P.: S. A. E. Journal **35**, No. 4, 359–69 (1934).
(79) WOODS, G M · Petroleum Engr. **8**, No. 3, 50–64 (1936).
(80) ZIEGENHAIN, W. T : Oil Gas J. **35**, No. 38, 11 (1937).
(81) ZIMMERMAN, J , AND MARTIN, F.: J. Chem. Phys. **23**, 747–87 (1926).

ECONOMICS OF KNOCK RATINGS OF OTTO-CYCLE ENGINE FUELS

P. C. KEITH, Jr., J. S. CAREY, AND J. T. WARD

The M. W. Kellogg Company, New York, New York

Any general consideration of the economics of the antidetonation properties of Otto-cycle engine fuels must include both automotive and aircraft fuels. While, as shown by table 1, in terms of absolute quantities consumed automotive fuels overshadow aviation fuels by a ratio of over 200 to 1, the latter are of increasing significance to the fuel manufacturer and of great importance in their economic bearing on modern transportation. In addition, development of high-octane blending agents for aviation fuels may profoundly influence automotive fuels. Owing to inherent differences in the requirements and the economic factors influencing the respective development of automotive and aircraft fuels, these two classes of fuels are necessarily discussed separately.

I. AUTOMOTIVE FUELS

The basis for the current octane ratings of automotive fuels is primarily with respect to performance, as indicated by the public's demand for rapid acceleration, freedom from gear shifting, etc. The demand has been met by the car manufacturers by increases in compression ratios, increases in engine speeds, better carburetion, and many relatively minor improvements. Supercharging of automobile engines has not come into widespread use, but its general adoption lies probably in the near future. All of these design factors could be directed toward fuel economy and lower specific engine weight per horsepower, but neither is in demand at present.

For these general reasons octane numbers of automotive fuels have been relatively stable over the past several years, as shown by table 2, but there is a trend upwards in the case of the premium-grade fuels. Regular-grade fuels have been artificially maintained at approximately 70 C.F.R.M. rating by the license provisions covering the use of tetraethyl lead in these fuels. If the contemplated change from the present C.F.R. motor test method results in raising the true or effective octane level, it may be expected that regular-grade fuels will immediately rise in octane number. In general, a gradual elevation in octane rating of automotive fuels may

be anticipated, with this gradual evolution susceptible to more sudden changes, not all of which can be forecast accurately. As will be discussed later, it is reasonable to suppose that, owing to the large potential supply of high-octane blending agents at present being developed for aviation

TABLE 1

Consumption of automotive fuels in the United States

YEAR	PREMIUM GRADE	REGULAR GRADE	THIRD GRADE AND MISCELLANEOUS	TOTAL
	gallons	gallons	gallons	gallons
1936	780,000,000	12,555,000,000	5,665,000,000	19,000,000,000
1935	619,000,000	11,399,000,000	5,232,000,000	17,250,000,000

Consumption of aviation gasoline in the United States (8)

YEAR	CONSUMPTION BY COMMERCIAL AIRLINES	CONSUMPTION BY GOVERNMENT SERVICES	MISCELLANEOUS	TOTAL CONSUMPTION
	gallons	gallons	gallons	gallons
1936	47,508,565		10,451,496	81,024,315*
1935	33,260,609	29,319,412	11,104,259	73,684,280
1934	25,136,274	23,647,113	9,630,869	58,414,256
1933	26,326,796	21,835,526	8,861,104	57,023,426
1932	23,686,948	20,077,884	10,293,599	54,058,431
1931	19,157,382		11,658,009	30,815,391
1930	14,549,477		13,981,331	28,530,808
1929	6,285,374		14,235,243	20,520,617
1928	2,134,690		7,764,702	9,899,392
1927	1,174,098		3,882,351	5,056,449
1926	863,617		2,246,028	

* Including estimated consumption by U. S. Government services.

TABLE 2

Average octane ratings of United States motor fuels (11)

YEAR (JAN. 1)	OCTANE NUMBER (C F R M.)		
	Premium grade	Regular grade	Third grade
1934	75	69	53
1935	75	69	52
1936	76	69	51
1937	77	70	54

fuels, some of this material may spill over into the automotive fuel market, thus creating new automotive fuels which will induce the development of engines capable of realizing their potentialities.

With the octane demand for automotive fuels relatively stable for the

moment in the 70 to 80 C.F.R.M. range, economic discussion will be directed toward the cheapest methods of producing these fuels.   Present automotive fuels (excluding third-grade gasolines) are blends of straight-run, reformed, cracked, and natural gasolines, with an increasing use of the newer polymer gasolines for further octane appreciation.   The use of tetraethyl lead to bring the finished blend to the final octane number is nearly universal.   Yearly quantities of motor fuel stocks segregated as to method of manufacture are given in table 3, in which it will be noted that in 1936 the volume of cracked gasoline exceeded that of straight-run for the first time.

With the majority of crudes, gasolines from gas oil or combination reduced crude cracking can be brought to octane levels where they present no difficult octane problems, at least in the manufacture of regular-grade gasoline.   Eliminating for the moment the use of polymer gasoline, the problem then reduces to the optimum economic utilization of the straight-

TABLE 3

Quantities, in barrels, of motor fuel stocks manufactured (9)

1 barrel = 42 U S. gallons

FUELS	1935	1936
Cracked	207,537,000	239,620,000
Straight-run	219,280,000	231,287,000
Natural	39,333,000	42,041,000
Benzol	1,871,000	2,537,000
Total	468,021,000	515,485,000

run material boiling in the gasoline range to permit its inclusion in the final blend.   The octane number of straight-run distillates may be raised by two principal methods: (*1*) naphtha reforming of all or a portion of the straight-run distillate, blending the reformed and virgin fractions, and leading to the required octane number, or (*2*) the use of tetraethyl lead alone.

Any economic comparison of the two general methods must compare the use of tetraethyl lead alone with the optimum combination of reforming plus ethylization.   The optimum combination of reforming and ethylization involves an economic balance to determine the percentage of the virgin straight-run gasoline to be reformed and the octane number and corresponding yield to be attained by the reforming operation to give the greatest return for the original raw material.

The assumptions used in these evaluations were as follows: (*1*) 70-octane finished gasoline has a transfer value of 6 cents per gallon.   (*2*) Fuel

(liquid or gas) valuation is 80 cents per 6,000,000 B.t.u. (L. H. V.). (*3*)
Evaporation and sweetening losses shall be held negligible. (*4*) The
octane and leading characteristics of a gasoline, whether sweetened or un-
sweetened, shall be considered identical. (*5*) Reforming cost shall be
assumed as 0.2 cent per gallon, charged to the reformer. Fixed charges
and royalty costs shall be omitted from consideration. (*6*) Sweetening
cost shall be assumed as 0.05 cent per gallon of gasoline sweetened. (*7*)
Virgin 100° to 400°F. base stock shall require no other treatment than
sweetening before leading. (*8*) No limitation of allowable tetraethyl lead
concentration in gasoline shall be considered as bearing upon the relative
economics of ethylizing and reforming. (*9*) Tetraethyl lead cost shall be
set at 0.26 cent per cubic centimeter, and costs of blending and mixing
with ethyl fluid shall be neglected. (*10*) No differential evaluation due to
varying vapor pressure or boiling range characteristic of finished gasoline
shall be made, and yields of reformed gasoline shall be based on 100 per
cent butane recovery. (This is a simplifying assumption and is usually
of minor importance.) (*11*) The evaluation of base stocks shall not take
into account lead credit or debit due to overall changes in lead consump-
tion resulting from blending with extraneous refinery gasolines. Evalua-
tions shall be based on the assumption that the lead requirements of a
blend of gasoline can be estimated with sufficient accuracy from a weighted
average of the lead requirements of the components raised to the same
octane number, where such lead requirements are small. (*12*) Evalua-
tions are to be distinguished from the ultimate values, which allow for
corrections involving the factors of casinghead price, refinery butane
balance, and lead susceptibility of the total gasoline produced in the
refinery.

The primary basis for comparative appraisal is a statement of the rela-
tion between raw charging stock value, finished gasoline value, leading and
sweetening costs when ethylizing the virgin straight-run to the required
octane. This relation is given by equation 1:

$$D = G - S - L \qquad (1)$$

where D = raw charging stock value (400° end point virgin gasoline) in
        cents per gallon, based on total ethylization,
    G = finished gasoline value in cents per gallon (70 C.F.R.M. or
        any other arbitrarily selected octane number on any fixed
        octane scale),
    S = sweetening cost, in cents per gallon sweetened, and
    L = leading cost of sweetened gasoline, in cents per gallon leaded.

The above calculation involved in evaluating the charge, D, in terms
of total ethylizing requires only ethylizing data and octane characteristics

of the 400°F. end point virgin naphtha and the basic transfer value of finished gasoline of the required octane (assumed in the illustrations cited as 6 cents per gallon).

The evaluation of 400°F. end point virgin gasoline in terms of optimum reforming plus ethylizing is the next step in the analysis. Assuming a basis of 1 gallon of 100–400°F. boiling range virgin charging stock, let:

C = charging stock value, in cents per gallon (100–400°F. virgin gasoline),

C_r = value of heavy naphtha to reformer, in cents per gallon,

C_v = value of raw virgin light naphtha, in cents per gallon,

G = gasoline value, in cents per gallon (70 C.F.R.M. sweetened gasoline or any other arbitrarily selected octane number on any fixed octane scale),

F = fuel value, in cents per gallon,

P = processing cost, in cents per gallon, charged to reforming,

L_v = leading cost of light virgin gasoline (to arbitrarily selected overall octane number), in cents per gallon leaded,

L_r = leading cost of reformed gasoline (to arbitrarily selected overall octane number), in cents per gallon leaded,

S = sweetening cost, in cents per gallon sweetened,

X = feed to reforming, per cent by volume of 100–400°F. charge, and

Y = yield from reforming (100 per cent C_4 recovery), per cent by volume of charge to reforming. Then

$$C_r = \frac{Y}{100}(G - S) + \left(\frac{100 - Y}{100}\right) F - P - \frac{Y}{100} L_r \qquad (2)$$

and

$$C_v = G - S - L_v \qquad (3)$$

but

$$C = \frac{X}{100} C_r + \frac{100 - X}{100} C_v \qquad (4)$$

and

$$C = \frac{X}{100}\left[\frac{Y}{100}(G - S) + \left(\frac{100 - Y}{100}\right) F - P - \frac{Y}{100} L_r\right]$$
$$+ \frac{100 - X}{100}(G - S - L_v) \qquad (5)$$

The above relationship of equation 5 allows for no correction factor for treating losses, since it is designed primarily for use with reforming set-ups

including clay treating and stabilization   Stock losses from treating and treating costs, as well, can be evaluated and included under the processing cost (P) to make the equation generally applicable.

TABLE 4

Comparison of values of 400° end point virgin naphtha, total ethylizing versus ethylizing and reforming

Optimum values and operating conditions

	SOURCE		
	Pennsylvania	Mid-Continent	East Texas
Light virgin naphtha:			
Volume per cent of 400° end point base naphtha ..	39 6	48 0	77 0
C.F R M. octane number	63 6	63 4	63.3
Heavy naphtha:			
Volume per cent of 400° end point base naphtha	60 4	52 0	25 0
C F R M octane number	29 2	32 2	29 6
Reformer yield, volume per cent of heavy naphtha	84 8	85 7	86.8
C F R.M octane number of reformed gasoline	65 0	65 4	63 5
Total gasoline:			
Yield, volume per cent of 400° end point base naphtha	90.8	92 5	97 0
C.F R.M. octane number* unleaded	64 5	64 2	63 3
Cc of lead per gallon to 70.0 octane number†	0 67	0 65	0.59
Cc. of lead per gallon to 70.0 octane number, straight leading without reforming	5 2	3 0	1.6
Value of 400° end point base naphtha:			
Value when leading only, in cents per gallon .	4 597	5 170	5.534
Value when leading and reforming, in cents per gallon	5 300	5 386	5.638

* Weighted average of octane numbers of light virgin naphtha and reformed naphtha.

† Weighted average of lead required for light virgin and reformed naphthas.

Equation 5 indicates a method for computing the values of charging stock in terms of ultimate gasoline value for any overall octane requirement and fuel evaluation for any combination of reforming and leading. It will be noted that certain basic data are necessary for the solution of these equations, including leading and octane characteristics of various percentages of light and heavy naphthas, and correlations covering the

reforming yields for the heavy naphthas considered when reformed to various octanes. A detailed presentation of all these data is beyond the scope of this paper, but the data on which the final results of figure 1 are based are summarized in table 4.

Figure 1 shows the results of applying an economic balance to determine the optimum combination of reforming and ethylizing for three typical
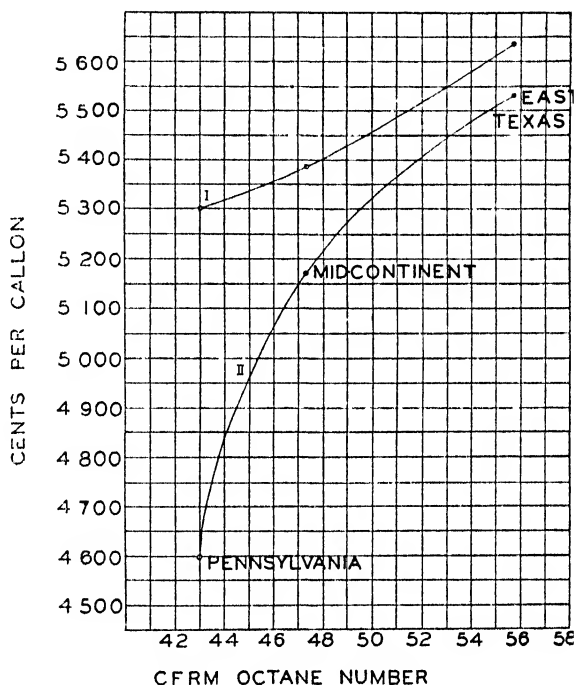
Fig. 1. Comparison of values of 400° end point virgin naphtha for leading only and for optimum reforming plus leading. Conditions: gasoline = 6 cents per gallon; fuel = 80 cents per barrel; lead = 0 26 cent per cubic centimeter; reforming cost = 0.2 cent per gallon charged. Value of 400° end point virgin naphtha, in cents per gallon, is plotted against C.F R.M. octane number of 400° end point virgin naphtha. Curve I, optimum ethylizing and reforming to 70 C F.R M. Curve II, ethylizing only to 70 C.F.R M.

400°F. end point straight-run gasolines as a comparison with the use of tetraethyl lead alone. Examining figure 1, it will be noted that the differential between the use of lead alone and the optimum combination of reforming and leading decreases with increase in octane of the original 400°F. end point base stock. It must be emphasized that the absolute values as shown in figure 1 are based on assumptions as noted, and that

any specific case must be subjected to a more extended analysis, taking into account all local conditions.

The economics of the manufacture of premium-grade automotive fuel are not as susceptible to general analysis, owing to the fact that the quantity of premium-grade gasoline produced by most refiners is small compared with that of regular-grade gasoline, and therefore selected stocks of higher than overall average octane are utilized. Polymer gasolines are finding increasing use in premium-grade blends. Table 5 illustrates the blending

TABLE 5

Ethylizing characteristics of refinery gasoline blended with thermal polymer gasoline

	OCTANE NUMBER BY C F R.M METHOD	TETRAETHYL LEAD TO 70 C F.R M	TETRAETHYL LEAD TO 78 C F R.M.
		cc.	cc.
Base stock (refinery blend). .	67 0	0.37	3.56
Polymer gasoline	77 0		
Blend of 70 per cent base and 30 per cent polymer .	71.0		1.15

TABLE 6

Thermal polymer gasoline as blending agent in preparation of premium automotive fuel
Basis: 70 gallons of base stock

	TETRAETHYL LEAD REQUIRED TO 78 C F.R.M.
	cc.
70 gallons of base at 3 56 cc. per gallon .	249
70 gallons of base and 30 gallons of polymer gasoline = 100 gallons of blend at 1.15 cc. per gallon	115
Tetraethyl lead equivalent per gallon of polymer ...	134

Premium value of polymer gasoline over 78-octane fuel based on tetraethyl lead at 0.26 cent per cubic centimeter = $(134 \div 30)$ cc. $\times$ 0.26 cent = 4.46 cc. $\times$ 0.26 cent = 1.16 cents per gallon

and leading characteristics of thermal polymer gasoline, when used as a blending agent in preparing premium-grade gasoline from a base stock of initially high octane number. From the data of table 5 the calculations of table 6 may be made, assuming that the total premium-grade fuel sold will be increased by the amount of polymer gasoline in the blend.

II. AVIATION FUELS

In comparison with the 70 to 80 C.F.R.M. octane range of automotive fuels, the present working range of fuel octane ratings used in commercial

air transport work is 80 to 90 C.F.R.M. Appreciable quantities of 100-octane fuel are being used for military and special purposes, and wide-spread commercial use of 90- to 100-octane fuels appears to lie in the immediate future. While no accurate data are available to indicate overall octane trends in aviation fuels, table 7 shows the proportions of the fuels of different octane ratings upon which the U. S. Army Air Corps has requested bids over a period of seven years. In the year ending July 1, 1937 the Army purchased 3,000,000 gallons of 100-octane fuel, and the 1937–38 purchases will show a substantial increase in the proportion of 100-octane fuel. The octane trend in the fuel purchases of commercial airlines has shown a similar upward swing. As the major United States airlines are at present operating nearly identical equipment, it is not surprising that the fuels used should fall in a narrow range with respect to octane requirements.

TABLE 7

Distribution of U. S. Army fuel purchases with respect to octane number (1)

YEAR	OCTANE NUMBER*				AVERAGE OCTANE NUMBER
	58–65	87	92	100	
	per cent	per cent	per cent	per cent	
1930	56 4	43.6			70.6
1931	31 6	68 4			77.7
1932	16 6	83.4			82 2
1933	6 5	50 2	43.3		87.3
1934	5.3		94 7		90.2
1935	3 9		91 7	4 4	91.3
1936	3 5		77 5	19.0	92.6

* Army method.

The newest type engines in the United States land transport service are for the most part using 87 to 90 C.F.R.M. octane fuel for both takeoff and cruising for the best overall economy. The immediate predecessors of these engines, which are still in service and far from obsolete, have been found to give good operating results on 87-octane fuel for takeoff and 80-octane fuel for cruising. Economic studies are being conducted by the various operators, balancing overall fuel and engine maintenance costs against the price differentials for the fuels of higher octane number. One large airline reports a definite economic justification for the use of 90-octane fuel throughout in its newest equipment as against 87-octane fuel. It may be concluded, therefore, that, compared with the relative stability of octane requirements for automotive fuels, aircraft fuels are in a state of change, with the choice of octane number determined by economics, based on the use of present equipment. The engine manufacturers are

now ready to offer engines which will be capable of taking full advantage of fuels up to 100-octane number or higher. The rapidity with which the new engines and fuels will be generally adopted is again entirely a question of economics.

Briefly examining current specifications for aircraft fuels, it will be noted that requirements other than octane number dictate largely the source of supply of the current fuels, and, to a large extent, the chemical constitution of these fuels. Table 8 summarizes typical specifications of large purchasers of aviation fuels in the United States. In general, these specifications tend to exclude, except in small blended concentrations, other than paraffinic types of gasoline. The present situation, owing to the maximum permissible tetraethyl lead concentrations, is that 87-octane grades can only be manufactured from carefully selected crudes. Therefore current demands dictate increasing use of the high-octane blending agents, if the octane trend is to continue upward.

Economic discussion of aviation fuels must attempt to answer the following questions: (1) What are the potential increased earning powers of fuels of higher octane number? (2) Will outlets other than 100+-octane aviation fuels absorb a portion of the high-octane blending agents? (3) What are the potential supplies of the high-octane blending agents?

The first question has been the subject of much technical discussion over the past several years. It is beyond the province of this paper to present the technical details involved in the evaluation of octane numbers in terms of engine performance and fuel saving. The major conclusions of these studies will be summarized briefly, following which their economic significance will be dealt with.

Klein (7), Buc and Aldrin (3), Du Bois and Cronstedt (4), Young (10), and others have presented the various relations between results obtainable with higher supercharge, higher compression ratios, and combinations of the two together with their relations to fuel consumption and the octane ratings of fuels. In general it may be stated that, for high maximum power output, high supercharge without very high compression ratio is desirable, whereas for maximum economy under cruising conditions high compression ratio is necessary

Barnard (2) has shown that present land transport designs are standardized at a total gross loading of approximately 13 lb. per brake horsepower available for takeoff. Disposable load (fuel, oil, crew, payload) for current designs, regardless of ship size, is approximately 34.5 per cent of the gross load or 4.5 lb. per brake horsepower available for takeoff. Higher loadings are permissible for sea operations, owing to the greater space available for takeoff. For example, the Trans-Pacific flying boats are reported to be designed for a disposable load per brake horsepower maxi-

mum of 6.7. It follows, therefore, that any increase in brake horsepower maximum (without appreciable increase in engine weight) will permit taking off with higher loads. The other means toward economy is by obtaining lower specific cruising fuel consumption. Barnard (2) has shown that a close balance exists between the economics obtainable by increasing boost (increasing takeoff horsepower) and decreasing specific fuel consumptions by increased compression ratios. Either route requires higher octane numbers. For commercial airline work a compromise is made between the two in engine design.

With a given engine design and fuel, current practice is to operate on a rich mixture for takeoff to obtain maximum power without detonation. At the conclusion of the takeoff period the throttles are partially closed and the mixture leaned to obtain cruising power output The extent to which the mixture can be leaned down safely under cruising conditions, and hence the specific cruising fuel consumption obtainable in actual operation, is only determined, for a given engine and fuel, by operating experience. Until recently mixture control was entirely based on the pilot's judgment, and, with the many details requiring his attention, the tendency was to operate on a cruising mixture which was safely on the rich side. One gauge of mixture control was formerly R.P.M., which is now no longer possible in actual service with constant-speed propellers. Another criterion of detonation during this recent period of development was cylinder head temperature. With the newer engines of higher specific output better cooling is required, which has resulted in invalidating the previous relationship between cylinder head temperature and harmful conditions in the cylinder. It is reported that with engines of the latest design pistons will be ruined, owing to detonating conditions, before abnormal cylinder head temperatures are indicated. Fortunately, instrumentation for mixture control has improved so that the mixture may be controlled to the known safe value either by automatic mixture control or manually, checked by exhaust gas analysis.

As a result of better engines, better fuels, and newer control devices, rapid strides have been made in lowering the specific cruising fuel consumption obtained in practice. Whereas a year and a half ago cruising fuel consumptions in commercial operation of the order of 0.55 lb. per brake horsepower hour were considered excellent, the same operators report that they are today realizing specific consumptions of 0.46 to 0.48 lb. per brake horsepower hour in their newest equipment and with present fuels of 87 to 90 octane number. The specific fuel consumption which may be anticipated in actual practice for fuels on the order of 100 octane number is a subject of some uncertainty. Tests (10) have been reported indicating that under carefully controlled conditions specific consumptions as low as 0.35 lb. per brake horsepower hour have been obtained.

TABLE 8

*Aviation gasoline specifications of typical U. S. consumers**

Column groups (consumer — grade / specification / date of last revision):

- **U. S. ARMY AIR CORPS** — Grade: 100, Spec. 2-92, Date of last revision: 6-20-35; Grade 92, Spec. 2-95, Date of last revision: 6-19-35
- **PRATT AND WHITNEY** — Grade: 506, 507, 511, Date of last revision: 9-8-33
- **WRIGHT AERONAUTICAL** — Grade: 5901 E, 5902 E, 5903 E, 5904, and 5905 A, Date of last revision: May, 1937
- **AMERICAN AIRLINES** — Grade: 720, 800, 801, 802, 872, 873, and 933, Date of last revision: 1-24-36
- **UNITED AIRLINES** — Grade Winter Antiknock, Date of last revision: 7-1-36
- **PAN-AMERICAN AIRWAYS** — Grade PAA 87 Octane, Date of last revision: 4-24-35
- **EASTERN AIRLINES** — Grade same as Wright with exceptions
- **T W A** — Grade: 73, 80, 87, and 90, Date of last revision 7-10-36

SPECIFICATIONS	Army G100 Max	Army G100 Min	Army G92 Max	Army G92 Min	P&W Max	P&W Min	Wright Max	Wright Min	American Max	American Min	United Max	United Min	Pan-Am Max	Pan-Am Min	Eastern Max	Eastern Min	TWA Max	TWA Min
Octane number	Not less than C.P. isooc-tane	Not less than C.P. isooc-tane	Not less than 72 parts iso-octane and 28 of n-heptane plus 3 cc of TEL			73, 80, 87		73, 80, 87, 90, 95	First two digits of grade numbers			74, 80, 83, 87		87				73, 80, 87, 90
Type of knock engine	C.F.R. 2-94 (Army)		C.F.R. 2-94 (Army)		C F R	C F.R M	C F R	C F.R M.	C F R	C F R M	C F R	C F.R M	C F R	C F R M	C F R	C F R ¶	C F R	C F R ¶
Knock test method																		
Pb(Et)$_4$ permitted, ml. per gallon	3.0		6 0		73, 80-2	87.3	1, 2, 3 / 3.75 / 4 00		Last digit grade Nos		80-2	83-87.3	2.5		80-1 5 / 87-3.0		73—none / 80-1.5 / 87-3 0 / 90-4 0	
Corrosion—copper dish	Must pass		Must pass		Must pass		Must pass		Must pass		Must pass		Must pass				Must pass	
Gum (Accel.—4 hr., 100°C., 100 # O$_2$)	10 mg.		10 mg		10 mg		10 mg		10 mg		10 mg		10 mg				10 mg.	
Color ...	Blue		Blue				W. W. before dye		Leaded—blue	Unlead-ed plus 25								
Acid heat °F					20		20 (b)		20		20						20	
Sulfur, per cent	0.10		0.10		0.10		0.10		0 10		0.10		0.10		0.10		0.10	
Reid vapor pressure, lb. per square inch	7.0		7.0		7.5		7.0		7 0		7 5		6 5				7.0	
Freezing point, °F.	−76		−76		−76		−76		−76		−76 (f)		−76				−76	
Distillation characteristics: 5% condensed, °F					150				150		140							
10% evaporated, °F (a)	167		167		167		167						167				167	

	1	2	3	4	5	6	7	8
10% condensed, °F		158		167	150			
50% evaporated, °F (a)	212	195	212	212	195	212	221	221
50% condensed, °F		231		266	231			
90% evaporated, °F (a)	275		275			275	347	347
90% condensed, °F		252		311	252			
90% condensed, °F								
Distillation loss			2 0	2.0	2.0			
Distillation residue	2.0	2.0	1 0	2 0	2 0		2.0	2.0
Recovery			96	96	96			
Sum 10, 50, 90% evaporated, rated	307	307	307	307			564	554
Sum 10, 90% evaporated		96			96	96		
Reaction 10% bottoms			Neutral		Neutral	Neutral		
Aromatic HC's permitted	Yes	Yes	Yes	Yes			Not required	Yes
Water tolerance	(c)		Yes	Yes		(g)		
Heat of combustion	(d)		(e)					
Odor	(h)							

* Compiled by Central Aviation Department, Standard Oil Development Company

(a) The per cent evaporated shall be found by adding the distillation loss to the amount collected in the receiver at each specification point.

(b) Subject to nitrating test The difference between the initial and final temperatures (maximum) shall not exceed 40°F. 20 cc of nitrating acid (75 per cent concentrated sulfuric and 25 per cent concentrated nitric acid by volume) is added to 50 cc. of the sample. This addition is made in a beaker drop by drop for the first few drops, if the reaction is not violent the balance of the acid may be added without this precaution. The mixture is then constantly stirred with a thermometer until the temperature drops and the maximum temperature is recorded as the final temperature. The initial temperature is that of the nitrating acid before it is added to the sample. The temperature of the gasoline before the acid addition is made shall not vary more than 1°F. plus or minus from that of the nitrating acid.

(c) Water tolerance: 80 ml of fuel shaken with 20 ml of water; on settling balance of water must neither increase nor decrease more than 2 ml

(d) The product of heat of combustion (high value) in B T.U. per pound by specific gravity shall not be less than 13,700.

(e) For 96 grade the heat of combustion or lower calorific value shall be not less than 20,500 B.T U. per pound as determined in an oxygen bomb calorimeter.

(f) Summer grade identical with winter grade except for 15 per cent point, which is 150° max.

(g) Note· The gasoline shall be a straight-run product

(h) The odor of the fuel shall not be nauseating or irritating. No substances of dangerous toxicity under usual handling shall be present.

On the other hand, it is reported that difficulty has been encountered when attempting to operate the newest engines with 100-octane fuel at 0.39 lb. per brake horsepower hour, and it is indicated that engine manufacturers will hesitate to guarantee 100-octane fuel engines for specific fuel consumption less than approximately 0.43 lb. per brake horsepower hour. Relative values for cruising specific fuel consumptions of 0.47 lb. per brake horsepower hour for 87-octane fuel and 0 40 lb. per brake horsepower hour for 100-octane fuel and engines have therefore been assumed in subsequent illustrations with the feeling that adequate credit is being given to the higher octane fuel.

Barnard (2) recently demonstrated the increased potential earnings obtainable by the use of the higher octane fuels, basing his calculations on data available on engine and fuel performance. While this analysis provided a stimulus to both the engine and the fuel manufacturers, it is felt that it fell short of indicating the probable economic value of the higher octane fuels to the commercial users of these fuels for the following reasons: (1) Increased earning power was computed on the basis of a fixed quantity of fuel   The same quantity of fuel of a higher octane number corresponds to a greater power development and hence an expanded operation. (2) Increased earning power as a function of fuel octane number was based on 100 per cent load factor, a condition never realized in practice, at least for land transport work in this country. (3) It was assumed that all of the potential increased payload due to the use of higher octane fuels could be realized and could be credited to the fuel with no overhead, profit, obsolescence or increased maintenance chargeable against the increased gross revenue. (4) No allowance was made for takeoff or reserve fuel.

The following illustration will attempt to show the effect of these factors on octane economic evaluation for a moderately long non-stop land transport operation in the United States. The trip chosen for the purposes of this study is one similar to the New York to Chicago non-stop flight conducted by several commercial airlines. While the figures used must be considered as approximate only, they are believed to be of the correct order of magnitude and that modifications of the basic premises will result in minor changes.

Table 9 summarizes the premises upon which subsequent calculations are based. In table 10 the minimum incremental value of 100-octane number fuel over 87-octane number fuel is calculated, based on lowered fuel consumption only. The maximum incremental value of 100-octane fuel versus 87-octane fuel is calculated in table 11 by assuming that all of the fuel weight saved can be replaced with revenue-producing payload.

To investigate the influence of load factor on the earning power of the higher octane fuel, it is necessary to examine the effect of load distribution,

i.e., for any given load factor the percentage of flights which go out fully loaded. Any given load factor (average percentage of full payload carried) can be attained with various distributions between full and partial loads.

Referring to figure 2, for illustration, if we assume a load factor of 75 per cent, this may be obtained with a distribution such that 40 per cent of the trips carry full load and 60 per cent partial load, the partially loaded flights averaging 58.3 per cent of full payload. Operation using 87-octane

TABLE 9

Premises for calculation of octane fuel valuations

Gross weight ship			24,000 lb.
Empty weight ship	.		15,600 lb.
Disposable load		...	8,400 lb.
Fuel (87-octane grade):	*Gallons*	*Pounds*	
Warm-up, taxiing and takeoff	25	150	
Climb, cruise and descent .	415	2,490	
Reserve .	100	600	
Total fuel .	540	3,240	
Oil .	43	322	
Crew (3)		500	
		4,062.	4,062 lb.
Payload			4,338 lb.

Specific cruising fuel consumptions:
   87-octane fuel, 0.47 lb. per brake horsepower hour
   100-octane fuel, 0.40 lb. per brake horsepower hour

Cost of 87-octane fuel (in plane tanks), per gallon	$0.13

Gross revenue: $0 0002875 per lb. mile ($5.75 per passenger mile with passenger plus baggage at 200 lb. average) To smooth the relationships payload and revenue are computed on a poundage basis.

Mileage (non-stop) .	720 mi.

fuel and engines based on this load factor and load distribution is defined by the solid line of figure 2.

With a given service between two points it is reasonable to postulate that increased revenue due to ability to carry added payload will only be realized during periods of peak demand, when present operations go out fully loaded and potential payload must be refused or extra ships (with partial payloads) operated. During the remainder of the period under consideration it is also reasonable to assume that the actual payloads

TABLE 10

Calculation of minimum incremental value of 100-octane over 87-octane fuel

Assumptions: (*1*) Fuel consumption for warm-up, taxiing, and takeoff is constant at 25 gallons (150 lb) irrespective of octane number. (*2*) Reserve fuel will be actually used on one-third of the flights. (*3*) The increased value per gallon of 100-octane fuel will be based on lowered consumption only.

87-octane fuel load . . .	3240 lb.
Takeoff, etc	150 lb.
Fuel for cruising and reserve . .	3090 lb
100-octane fuel for cruising and reserve:	
(0 40 ÷ 0 47) × 3090	2630 lb.
Takeoff, etc	150 lb.
100-octane fuel load	2780 lb.
Average fuel consumption of 87-octane fuel·	
3240 − ⅔ (600) = 2840 lb	473.3 gal.
Average fuel consumption of 100-octane fuel:	
2780 − ⅔ (600) × $\frac{0.40}{0\ 47}$ = 2440 lb	406 6 gal.
Total average cost of 87-octane fuel per trip:	
473.3 × $0.13 = .	$61 53
On the basis of equal fuel costs the minimum value, per gallon, of	
100-octane fuel = $61.53/406 6 .	$0.1513
Minimum incremental value, in cents per gallon	2.13

TABLE 11

Calculation of maximum incremental value of 100-octane versus 87-octane fuel

Assumptions: (*1*) Fuel consumption for warm-up, taxiing and takeoff is constant at 25 gallons (150 lb.) irrespective of octane. (*2*) Reserve fuel will be actually used on one-third of flights. (*3*) Ships go out fully loaded, i.e , 100 per cent load factor. (*4*) The fuel is credited with all of the increased gross revenue obtained by using the higher octane fuel.

Total load of 87-octane fuel . .	3240 lb.
Total load of 100-octane fuel ..	2780 lb.
Weight saving useful for payload	460 lb.
Increased gross revenue (100 per cent load factor):	
460 × 720 × $0 0002875 . .	$95.22
If the increased gross revenue is all credited to the fuel, the	
maximum value of the 100-octane fuel is 61.53 + 95.22	$156 75
Average consumption of 100-octane fuel .	406.6 gal.
Maximum value of 100-octane fuel per gallon = 156.75/406 6 .	$0 3855
Assumed price of 87-octane fuel .	0 130
Maximum differential price per gallon	$0.2555

realized will be identical, regardless of the fact that the ships used have an increased potential payload-carrying capacity. (These premises will furnish a picture of the increased earning power of the new fuels and engines in the period immediately following their adoption. Over a period of years, based on an expanding traffic, the probable ultimate increased earning power will be greater. It is the writer's belief, however, that economic justification must be based on present traffic demands and equip-
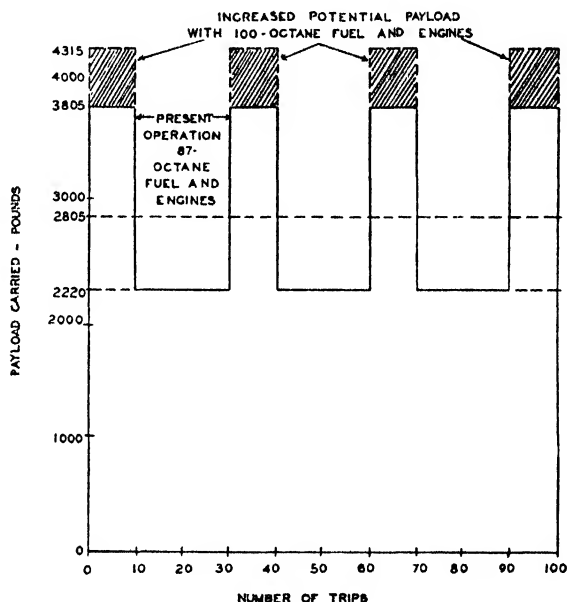
FIG. 2. Influence of load distribution on potential payloads, using 100-octane fuel and engines. Basis: 75 per cent load factor; 40 per cent of flights fully loaded; 60 per cent partially loaded. 4315 lb. maximum payload using 100-octane fuel and engines; 3805 lb. maximum payload present operation; 2805 lb. average payload present operation (75 per cent of 3805 lb.); 2220 lb average payload partially loaded flights (58 3 per cent of 3805 lb.).

ment. On the other hand, the installation of new engines in present ships will not impose an obsolescence charge against the new fuel and motors based on the present rate of engine replacement.)

The shaded areas in figure 2 represent the potential increased payloads which can be realized in whole or in part for the assumed load factor and distribution by the use of 100-octane fuel and engines.

The calculations of tables 10 and 11 have shown, respectively, the minimum and maximum increased values per gallon of 100-octane fuel

TABLE 12

Calculation of effect of load distribution on increased earnings with 100-octane fuel and engines

Basis: payload capacity 87-octane fuel and engines 4338 lb ; payload capacity 100-octane fuel and engines 4798 lb.

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)
			87-OCTANE FUEL AND ENGINES				100-OCTANE FUEL AND ENGINES							
NUMBER OF FLIGHTS FULLY LOADED	NUMBER OF FLIGHTS PARTIALLY LOADED	PER CENT OF FULL PAYLOAD ON PARTIALLY LOADED FLIGHTS	Payload carried on fully loaded flights	Payload carried on partially loaded flights	Total average payload per 100 trips	Gross revenue for 100 trips	Payload carried on fully loaded flights	Payload carried on partially loaded flights	Total average payload per 100 trips	Gross revenue for 100 trips	INCREASED REVENUE WITH 100-OCTANE FUEL AND ENGINES OVER PRESENT	MAXIMUM VALUE OF 100-OCTANE FUEL, 40,660 GALLONS	MAXIMUM VALUE OF 100-OCTANE FUEL	INCREASED VALUE OF 100-OCTANE FUEL OVER 87-OCTANE
		per cent	lb	lb	lb.	dollars	lb	lb	lb	dollars	dollars	dollars	cents per gallon	cents per gallon
							75 per cent load factor							
0	100	75	0	325350	325350	67347	0	325350	325350	67347	0	6153	15.13	2 13
20	80	68 8	86760	238590	325350	67347	95960	238590	334550	69252	1905	8058	19.82	6 82
40	60	58 3	173520	151830	325350	67347	191920	151830	343750	71156	3809	9962	24.50	11 50
60	40	37 5	260280	65070	325350	67347	287880	65070	352950	73061	5714	11867	29 18	16 18
75	25	0	325350	0	325350	67347	359850	0	359850	74489	7142	13295	32 69	19 69
							50 per cent load factor							
0	100	50	0	216900	216900	44898	0	216900	216900	44898	0	6153	15 13	2 13
20	80	37.5	86760	130140	216900	44898	95960	130140	226100	46803	1905	8058	19 82	6.82
40	60	16 7	173520	43380	216900	44898	191920	43380	235300	48707	3809	9962	24 50	11.50
50	50	0	216900	0	216900	44898	239900	0	239900	49659	4761	10914	26 84	13 84

* Sample calculations: Columns 1 and 2, basic premises. Column 3: for 75 per cent load factor, 20 flights out of 100 fully loaded.
Let X = per cent of full payload on partially loaded flights $20 + 80X/100 = 75$ $X = 68.8$ per cent. Column 4: column 1 × 4338 lb. Column 5: 4338 lb. × (column 3/100) × column 2. Column 6: column 4 + column 5. Column 7: 720 miles × $0.0002875 × column 6. Column 8: column 1 × 4798 lb Column 9: same as column 5. Column 10: column 8 + column 9. Column 11: 720 miles × $0.0002875 × column 10. Column 12. column 11 – column 7 Column 13: cost of 87-octane fuel for 100 trips ($61.53 × 100) + column 12. Column 14: column 13 ÷ 40,660 gallons Column 15: column 14 – 13 cents.

over 87-octane fuel for the given set of premises. The probable answer lies somewhere between the two. Table 12 shows a calculation of increased earnings for 100-octane fuel based on 75 and 50 per cent load factors but with various distributions between fully and partially loaded flights, and assuming that all the increased payload capacity under peak demand conditions can be realized. While the results of table 12 can be computed much more simply, this sample calculation is given in detail to avoid confusion as to the method employed.

Figure 3 summarizes the results of all calculations illustrated by table 12. Curve I of figure 3 defines the maximum incremental value,
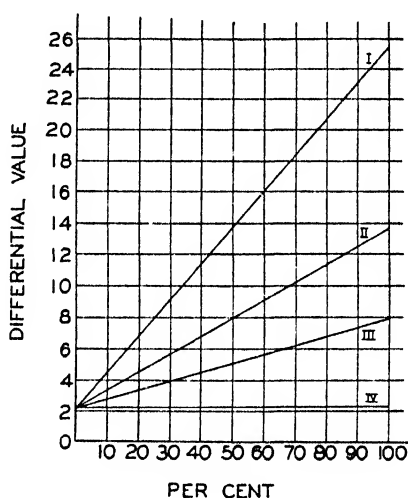
Fig. 3. Influence of load distribution on incremental value of 100-octane fuels. Differential value of 100-octane fuel over 87-octane fuel, in cents per gallon, plotted against per cent of flights fully loaded. Curve I, assuming all of potential increased payload credited to fuel; curve II, 50 per cent of potential increased payload credited to fuel; curve III, 25 per cent of potential increased payload credited to fuel; curve IV, no increased payload credited to fuel.

for any load factor and load distribution, of 100-octane fuel and engines over 87-octane fuel. If we take, for example, a 75 per cent load factor, obtained with a distribution of 75 per cent of the flights fully loaded and 25 per cent with zero load, an incremental value of 19.7 cents per gallon is read from figure 3, which represents the maximum differential value obtainable for 100-octane fuel with an overall load factor of 75 per cent. If, with a load factor of 75 per cent, only 40 per cent of the flights are fully loaded, the incremental value is depreciated to 11.5 cents per gallon. If 0 per cent of the flights are fully loaded and 75 per cent partially loaded,

an incremental value of 2.1 cents per gallon is obtained, corresponding to the reduced fuel consumption only. A 100 per cent load factor obviously means 100 per cent of flights fully loaded.

Curve I of figure 3 assumes that all of the increased potential payload-carrying capacity can be sold during periods of peak demand. It is believed to be a fair approximation to assume that an average of only 50 per cent of the increased payload capacity can be realized. On this basis the curve designated as II becomes the reference curve.

Figure 3, as discussed so far, really refers to probable increased gross earning per gallon of fuel. The net increased earning power per gallon for the higher octane fuel will be less than the increased gross earning by the amount of the fixed charges against this increased revenue. The increased revenue per gallon which can be credited to the fuel for higher price justification will therefore probably approximate 25 per cent of the total increased potential revenue earned by the use of the fuel. For the

TABLE 13

Approximate estimated increased earning power per gallon of 100-octane fuel over 87-octane for a 720-mile land transport operation

PER CENT OF FLIGHTS FULLY LOADED	CENTS PER GALLON DIFFERENTIAL
0	2.1
20	3.3
40	4.4
60	5.5
80	6.7
100	7.9

type of operation and on the basis of the premises used in this illustration, it would appear that differential net earning powers approximately as shown in table 13 could be postulated for 100-octane over 87-octane fuel for the various load distributions with probable differential earning powers falling in the range of 3 to 6 cents per gallon as shown by curve III, figure 3.

Curve IV defines the minimum incremental value of the higher octane fuel based on lower fuel consumption only and independent of load distribution.

It should be emphasized that the illustration here used is based on a long non-stop land operation. For shorter range operations the incremental value of higher octane fuel will be less, approaching the minimum incremental value of approximately 2 cents per gallon. On the other hand, the long range sea operations will show greater increased earnings for any increase in payload, but, again, the load factor and load distribution will reduce the premium which can be paid for the higher octane fuel.

III. ECONOMICS OF THE USE OF HIGH-OCTANE BLENDING AGENTS

The high-octane blending agents now available commercially as typified by isoöctane (2,2,4-trimethylpentane) and its isomers, and isopropyl ether, can be utilized in various ways as dictated by economic considerations: (*1*) as blending agents with aviation base stock for the manufacture of 100+-octane aviation gasoline; (*2*) as blending agents in the manufacture of 87-octane aviation gasoline; and (*3*) as blending agents in the manufacture of motor fuels, either 70-octane regular grade or ethyl grade.

The manufacture of 100+-octane aviation fuels with a tetraethyl lead maximum imposed by specifications makes the use of high-octane blending agents necessary. It has been demonstrated earlier that 100-octane fuels can probably command a price differential over 87-octane fuels in the range

TABLE 14

Octane numbers and tetraethyl lead response of isopropyl ether and isoöctane blends with aviation base (3)

BLENDING AGENT	VOLUME PER CENT ADDED	CLEAR	A.S.T.M. OCTANE NUMBERS	
			1 cc. of tetraethyl lead per gallon	3 cc. of tetraethyl lead per gallon
Isopropyl ether	0	73.5	82.0	87.5
	10	76.3	84.1	89.3
	25	80.5	88.6	94.0
	40	85.0		97.5
Isoöctane	0	73.5	82.0	87.5
	10	76.0	84.0	89.0
	25	79.4	86.8	91.4
	40	83.0		94.2
	50	85.5	93.0	96.0

of 3 to 6 cents per gallon if used in the longer range land transport work in the United States. Considering that the blended fuels will probably not contain over 50 per cent of total blending agent, a price differential of this order should assure the manufacturers of sufficient "spread." The writers estimate the approximate manufacturing cost of any of the blending agents mentioned as falling in the range of 7 to 9 cents per gallon (including plant depreciation at 20 per cent per year and charging stock debited against the operation at 15 cents per million B.t.u. with corresponding fuel oil credits for by-products).

Table 14 gives published C.F.R.M. octane numbers of isopropyl ether and isoöctane blends together with leading characteristics.

Assuming an 87-octane aviation gasoline (containing 3 cc. of tetraethyl lead per gallon) and further assuming that a blend of this aviation gasoline

with 40 per cent of an hypothetical blending agent will furnish 100-octane gasoline (the blend also containing 3 cc. of tetraethyl lead per gallon), the relation between the values of 87-octane aviation gasoline and the blending agent is calculated in table 15.

Aviation gasoline of 87 octane number is being prepared from selected straight-run light naphthas without exceeding lead tolerances imposed by specifications. The economic value of the high-octane blending agents in the preparation of 87-octane gasoline can be based on: (1) the lead replacement value using the present selected base stocks, and (2) the upgrading of straight-run naphthas of lower octane than the present selected base stocks. Examining the first possibility, and using blending and leading

TABLE 15

Value of high-octane blending agents in manufacturing 100-octane aviation gasoline

Basis: aviation gasoline of 87 5 C.F.R M. octane number containing 3 cc. of tetraethyl lead per gallon

Assumed blend: 60 per cent of 87 5-octane aviation gasoline and 40 per cent of blending agent. Assume that the blend with 3 cc of tetraethyl lead per gallon will have 100 octane number. Let A = value of 87 5-octane base in cents per gallon, B = value of blending agent in cents per gallon, and P = premium value of 100-octane over 87-octane in cents per gallon:

$$0.6A + 0.4B = A + P$$

$$B - A = \frac{P}{0\ 40} \quad \text{(equation 6)}$$

Value of P cents	Value of $B - A$ cents
2	5
4	10
6	15
8	20

data as given by Buc and Aldrin (3), the calculations of table 16 may be made.

If the high-octane blending agents were used in the manufacture of 87-octane fuels, a much lower premium based on lead saving would be obtained for the blending agent than when used in the manufacture of 100+-octane. (This illustration assumes that the 87-octane unleaded isoöctane blend would give the same performance as an 87-octane fuel containing lead. Evidence indicates that a leaded fuel would rate higher in performance on a full scale engine test.)

The use of high-octane blending agents in upgrading low-octane straight-run naphthas, thereby making them available for use in 87-octane aviation blends, is illustrated in table 17.

TABLE 16

Value of high-octane blending agents on lead replacement basis in making 87-octane aviation gasoline

Octane number of aviation gasoline base plus 3 cc of tetraethyl lead	87 5
Lead required, cc. per gallon, to raise 25 per cent isoöctane blend to 87.5-octane aviation gasoline	1 05
Basis—gallons of 87.5-octane aviation gasoline	75
Aviation base stock, 75 gallons at 3 cc of tetraethyl lead per gallon	225 cc.
Blend: 100 gallons (75 gallons of aviation base + 25 gallons of isoöctane) at 1 05 cc of tetraethyl lead per gallon	105 cc
Tetraethyl lead equivalent of 25 gallons of isooctane .	120 cc.
Cc of tetraethyl lead per gallon of isoöctane .	4 8
Cents per gallon differential value of isoöctane over 87 5-octane aviation gasoline, based on tetraethyl lead saving, equals 4 8 × 0.26 cent	1 25

TABLE 17

Value of high-octane blending agents in upgrading low-octane naphtha to furnish aviation base

Assume a straight-run naphtha of 65 octane number. This material will be upgraded by the use of a 100-octane blending value blending agent to match a 73 5-octane aviation base stock   The aviation base and the blend can each be brought to 87 octane by the use of 3 cc of tetraethyl lead per gallon

Preparation of blend: Let X = percentage of 65-octane naphtha in blend

$$65\frac{X}{100} + \left(1 - \frac{X}{100}\right)100 = 73.5$$

$X = 75\ 7$ per cent of 65-octane straight-run naphtha

Let A = value of 87-octane aviation base in cents per gallon, B = value of blending agent in cents per gallon, and N = value of 65-octane naphtha in cents per gallon:

$$0\ 757N + 0\ 243B = A - 3 \times 0\ 26$$

$$B = 4\ 11A - 3.11N - 3.21$$

$$B - A = 3.11(A - N) - 3.21 \qquad \text{(equation 7)}$$

Values of $A - N$ cents	Values of $B - A$ cents
3	6
6	15

For differential values of 87-octane aviation over 65-octane straight-run naphtha of 3 or 6 cents per gallon, the corresponding premium values of the blending agent over 87-octane aviation become approximately 6 and

15 cents per gallon, respectively; hence this use of the high-octane blending agents would appear to offer economic possibilities.

The few data available on the blending and leading characteristics of the high-octane blending agents are for the most part confined to blends with straight-run naphthas suitable for aviation base stocks or with the various standard reference fuels. The octane blending and leading characteristics of several of the high-octane blending agents may be sum-

TABLE 18

Use of high-octane blending agent (assumed blending value 100) in automotive fuel blend
Base stock: refinery blend as given in table 5

(A) Lead replacement value for 70 C.F.R.M. blend:

Let X = per cent of base stock in blend

$$67.0 \frac{X}{100} + 100 \frac{(100 - X)}{100} = 70.0$$

X = 91.0 per cent base stock

91 gallons of base at 0.37 cc. of tetraethyl lead per gallon .	33.6 cc.
100 gallons of blend (91 gallons of base + 9 gallons of blending agent) .	0.0 cc.
Tetraethyl lead equivalent to 9 gallons of blending agent	33 6 cc.
Cents per gallon premium value of blending agent over 70-octane = (33.6 + 9) × 0.26..	0 97

(B) Lead replacement value for 78 C.F.R.M. blend:

Let X = per cent base stock in blend

$$67.0 \frac{X}{100} + 100 \frac{(100 - X)}{100} = 78.0$$

X = 66.7 per cent base stock

66.7 gallons of base at 3.56 cc. of tetraethyl lead per gallon.. . . 238 cc.	238 cc.
100.0 gallons of blend (66.7 gallons of base + 33.3 gallons of blending agent)	0 cc.
Tetraethyl lead equivalent to 33.3 gallons of blending agent .	238 cc.
Cents per gallon premium value of blending agent over 78-octane = (238 + 33.3) × 0.26	1.85

marized as follows: (*1*) 2,2,4-trimethylpentane has an octane blending value of 92 to 100, with the lower blending values corresponding to the lower concentrations of the blending agent. The octane level of the blend appears to have little influence. The lead susceptibility of the blend is approximately that of the base stock, at least for the lower concentrations. (*2*) The other trimethylpentanes have octane blending values slightly lower than those of the 2,2,4 compound. The clear octane num-

ber approximates 95 as compared with 100 for c. p. isoöctane. (*3*) The dibutylenes or dimers before hydrogenation to the isoöctanes have octane blending values which are a function of concentration in the blend and octane level of the blend. Egloff (5) cites blending values varying from 152 (5 per cent concentration) to 95 (75 per cent concentration) when blended with A-3 Reference Fuel (43.6 octane number). (*4*) Isopropyl

TABLE 19

Use of high-octane blending agent (assumed blending value 130) in automotive fuel blend
Base stock: refinery blend as given in table 5

(A) Lead replacement value for 70 C.F R.M. blend:

Let X = per cent of base stock in blend

$$67.0 \frac{X}{100} + \frac{(100 - X)}{100} 130 = 70 \ 0$$

$X = 95.2$ per cent base stock

95 2 gallons of base at 0 37 cc. of tetraethyl lead per gallon	35.2 cc.
100.0 gallons of blend (95 2 gallons of base + 4.8 gallons of blending agent)	0 cc.
Tetraethyl lead equivalent to 4 8 gallons of blend	35.2 cc.
Cents per gallon premium value of blending agent over 70-octane = (35.2 ÷ 4.8) × 0.26	1.91

(B) Lead replacement value for 78 C.F R.M. blend:

Let X = per cent of base stock in blend

$$67 \ 0 \frac{X}{100} + \frac{(100 - X)}{100} 130 = 78.0$$

$X = 82.5$ per cent base stock

82.5 gallons of base stock at 3.56 cc. of tetraethyl lead per gallon	293.7 cc.
100.0 gallons of blend (82.5 gallons of base + 17.5 gallons of blending agent)	0.0 cc.
Tetraethyl lead equivalent to 17 5 gallons of blending agent	293.7 cc.
Cents per gallon premium value of blending agent over 78-octane = (293.7 + 17.5) × 0.26	4.36

ether has a blending value somewhat over 100 with concentration and octane level of the blend having little influence.

Based on these approximate data, the economics of the use of the high-octane blending agents are illustrated by tables 18 and 19.

From tables 18 and 19 it appears that the high-octane blending agents have low economic value when used for 70-octane automotive blends. In

the manufacture of premium automotive blends the blending value of the dibutylenes appears to give these materials an attractive economic value for the following reasons: Selective polymerization plants will produce good yields of dibutylenes based on the olefins charged. To manufacture the isooctanes hydrogenation is a costly further step in the process. Hence excess polymerization capacity over that required for the aviation blending agent may be installed, and the excess dimer produced may be blended in premium-grade motor fuel, thus permitting the processing of the aviation gasoline requirements only through the hydrogenation stage and realizing an attractive premium on the balance of the high-octane polymer.

IV. POTENTIAL SUPPLIES OF HIGH-OCTANE BLENDING AGENTS

The U S. consumption of aviation gasoline, as given in table 1, has been estimated as approximately 81,000,000 gallons for 1936. (The figures of table 1, while prepared from all available statistical data, may be somewhat on the low side) Based on the rate of increase for the past several years, the 1937 consumption will be in excess of 100,000,000 gallons. The world consumption of aviation gasoline for 1936 has been estimated by others at 252,000,000 gallons (6).

A survey of present available material for the manufacture of technical isoöctane (2,2,4-trimethylpentane) indicates a potential U. S. supply of 155,000,000 gallons per year (3). The potential supply of isomeric trimethylpentanes having octane ratings only slightly below that of 2,2,4-trimethylpentane must be appreciably greater than that of this compound, as the first step in their manufacture is the selective polymerization of isobutene and normal butene, resulting in "dimer" yields of 150 to 200 per cent of the isobutene content of the charge. Supplies of propylene for the manufacture of isopropyl ether have been estimated as sufficient for the U. S. manufacture of 340,000,000 gallons per year of technical isopropyl ether (diisopropyl ether) (3). It should be noted that any of these materials is at present only used in blended concentrations up to approximately 50 per cent.

From these figures it is evident that the potential quantities of several high-octane blending agents are far in excess of probable requirements for aviation gasoline; hence these materials may spill over into the motor fuel market for use in motor fuel blends if economic justification can be shown.

Other materials than the particular blending agents cited may be expected to influence aviation gasoline economics and octane ratings. The increased use of certain of these may be contingent upon revision of present specifications, particularly a clarification of fuel ratings in the region above 87 octane number with respect to actual engine performance.

V. CONCLUSIONS

1. Automotive fuels have been relatively stable in octane ratings for several years, with certain factors indicating a more rapid rise in octane number.

2. One of the major economic problems in the manufacture of automotive fuels is the most economical use of the straight-run naphtha fraction of the crude. With low-octane virgin naphthas the optimum balance is partial reforming and partial ethylizing, with the differential between partial reforming and total ethylizing decreasing with increased octane number of the virgin naphtha.

3. Aviation fuels are in a state of change with respect to octane numbers. The industry is ready to use 100+-octane fuels provided these are made available at a price structure permitting their economic justification by the users and as soon as engine manufacturers offer engines.

4. Based on certain premises it is the writers' belief that net increased earning powers of 100 effective octane aviation fuel over 87-octane fuel of 3 to 6 cents per gallon can be justified for a portion of the land transport work in the U. S. If all commercial U. S. land transport operations are included, the differential earning power will fall in the range of 2 to 6 cents per gallon.

5. It appears that the high-octane blending agents cannot be economically used in blends with aviation base stocks (of 73 to 74 C.F.R.M.) for the manufacture of 87-octane aviation gasoline. The high-octane blending agents can be used economically in upgrading low-octane naphthas for use in 87-octane aviation gasolines.

6. The use of the high-octane blending agents in automotive fuels would appear to be limited to those showing high blending values and in the manufacture of premium-grade automotive fuels. It is suggested that excess dibutylenes may be absorbed in premium-grade automotive fuel.

REFERENCES

(1) ALDEN AND PARKER: Oil Gas J. **36**, No. 1, 72 (1937).
(2) BARNARD: Paper presented before the National Aeronautic Meeting, S. A. E., March 11, 1937: also Natl. Petroleum News **29**, 65 (1937).
(3) BUC AND ALDRIN: S. A. E. Journal (Trans.) **39**, No. 3, 333 (1936).
(4) DuBois AND CRONSTEDT: Paper presented at the Annual Meeting of the Society of Automotive Engineers, January, 1937.
(5) EGLOFF: Ind Eng. Chem. **28**, No. 12, 1461 (1936).

(6) HOFFMAN, LAPEYROUSE, AND SWEENEY: Paper delivered at the World Petro-
    leum Congress, Paris, June, 1937.
(7) KLEIN: S. A. E. Journal (Trans.) **39**, No. 2, 304 (1936).
(8) NORMAN: Oil Gas J. **38**, No. 1, 64 (1937), and private communication.
(9) U. S. Bureau of Mines, Statistical and Economical Survey, Monthly Petroleum
    Statement No 154, February 11, 1937.
(10) YOUNG: S A. E. Journal (Trans.) **38**, No. 6, 234 (1936).
(11) ZIEGENHAIN: Oil Gas J. **35**, No. 38, 9 (1937).

DISCUSSION

J. EDWARD KLINE (Research Laboratories of the Standard Oil Company, Whiting, Indiana): This paper parallels Barnard's (Barnard: S. A. E. Journal (Trans.) **41**, No. 3, 415 (1937)) in its economic evaluation of octane number increases in aviation fuel.   Both papers justify a definite premium for higher octane fuels, but they differ considerably, first as to the basis employed and second, as to quantitative values cited for differential value determinations.

Barnard presents an evaluation expressed in terms of maximum increase in ultimate gross earning capacity per unit increase in octane number, 2.2 cents per octane number per gallon representing an average value, which he offers to substantiate his conclusion that the aviation industry must prepare for an increasing utilization and the petroleum industry for an increasing production of higher octane aviation fuels.   These incremental values are computed for revenue increases attributable either to the higher compression ratio or greater supercharge made possible by octane number improvement in the 72 to 100 octane range for flights of various duration. While it is more complete than the present paper in these respects, and while ample evidence is submitted to justify the conclusion mentioned above, Barnard's paper does not satisfactorily indicate either the immediate or the probable ultimate value of the higher octane fuels to their commerical users, because quantitative determinations are based on 100 per cent load factor and on equipment designed to take the fullest possible advantage of octane improvements, and because revenue increases are given in terms of gross rather than of net earning capacity.

The economic evaluation given in the present paper is confined to a single illustration of the immediate increase in net earning capacity of 100-octane over 87-octane fuel and engines when used in present planes. The authors allow additional payload only during those periods of peak demand when present ships go out fully loaded, and conclude that a value of 0.2 to 0.5 cents per octane number per gallon is probably justifiable. This does not recognize the validity of postulating an increasing utilization of higher octane fuels on the basis of their probable ultimate increased earning capacity.   It seems that the true evolutionary character of such

a shift in fuel specifications is not appreciated, for, whereas only a few operators may find it immediately advantageous to incorporate 100-octane fuel and engines in their present planes on the basis of incremental values cited, eventually the collaboration of fuel manufacturers, airplane and engine designers and builders, and airline operators will make possible full realization of the ultimate increased earning capacities of the higher octane fuels. Whether it be by normal expansion in traffic or by obsolescence or both, airline operations using 100-octane fuel will be made fully as suitable for then existing conditions as is 87-octane fuel for the present.
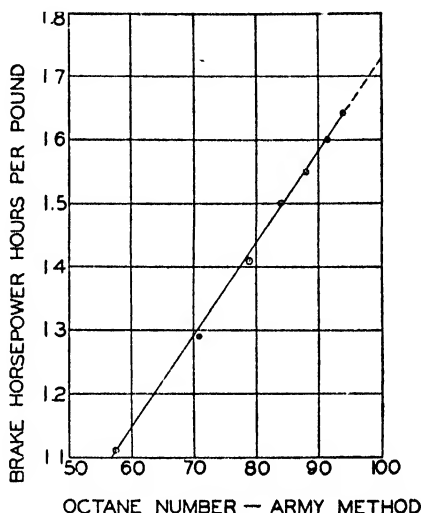
Fig 1. Plot of engine efficiency versus fuel octane number. Data obtained on the Army C.F.R. engine. The curve holds for fuels of the same calorific value as iso-octane.

It would seem more reasonable for the present paper to compare 87- and 100-octane fuels on the basis of identical load factors for the given operation, if the resulting values are to serve as a criterion for indicating the probable future of high octane number aviation fuels. While the values cited by Barnard represent the most optimistic outlook, those given in the present paper should be regarded as representing an unjustifiably pessimistic viewpoint. It would appear that a more conservative outlook could be based on an average load factor of 60 per cent, for which differential values between 1 and 1.5 cents per octane number per gallon are more nearly indicative of the probable ultimate increased earning capacities of higher octane fuels.

F. L. GARTON (Shell Petroleum Corporation, Wood River, Illinois):[1] With the advent of transoceanic flights, the importance of high-octane fuels is increasing rapidly, and the authors' remarks on the economics of these fuels are very timely. In this connection I should like to explode a fallacy which has been current during the last few years. It is often stated that octane numbers are larger, the higher in the octane range one goes. It is true that an increase from 85 to 90 octane number will allow a greater increase of compression ratio than an increase from 45 to 50 octane number. However, the curve of thermal efficiency versus compression ratio falls off at the higher ratios and tends towards a maximum. The net result is that the efficiency is roughly a linear function of fuel octane number over the practical range. This is shown in the attached figure, in which the efficiency, expressed as brake horsepower hours per pound of fuel, is plotted against fuel octane number. This curve is derived from data obtained on the Army C.F.R engine and holds for fuels of the same calorific value as isooctane.

It will be noted that the curve is sensibly linear and does not show signs of approaching a maximum. The possible increase in efficiency on changing from an 87- to a 100-octane fuel is indicated to be about 11.5 per cent. However, it has been shown by Barnard (S.A E. Journal (Trans.) 32, 418 (1937)) and others that in this high octane range greater improvements in efficiency can be obtained by supercharging than by increasing the compression ratio.

[1] Received September 18, 1937.

THE KINETICS OF ELEMENTARY REACTIONS OF THE SIMPLE HYDROCARBONS

E. W. R. STEACIE

Physical Chemistry Laboratory, McGill University, Montreal, Canada

CONTENTS

I. INTRODUCTION

The reactions of the simple hydrocarbons are of great importance from both the theoretical and the industrial points of view. From a theoretical standpoint tremendous strides have been made in the past decade. Ten years ago little was known about the mechanisms of the simple thermal reactions, in spite of the fact that an enormous mass of purely pyrolytic data had been accumulated. In the last few years the subject has advanced rapidly, owing to the application of the methods of chemical kinetics, to the investigation of atomic and photosensitized reactions, and to enquiries into the rôle played by free radicals in thermal reactions. While there is considerable doubt regarding the validity of some of his speculations, there is no question that the ideas of F. O. Rice regarding the participation of free radicals in thermal processes have given a tremendous stimulus to the investigation of hydrocarbon and other reactions.

Owing to the complexity of the subject, the many angles from which it may be approached, the rapidity of its development, and the scattering of papers through organic, physical, and industrial journals, it is very difficult to orientate oneself in this field. Numerous reviews have appeared on hydrocarbon chemistry, but they have all been concerned primarily with the products of the reactions from an industrial standpoint. The theoretical basis of the subject must, however, rest on the principles of chemical kinetics, and a review of existing kinetic data from this point of view seemed desirable to the writer. In this review an attempt has been made to include all data which seem to be pertinent to the kinetic analysis of the simple thermal and photochemical reactions of the lower paraffins, olefins, and acetylenic hydrocarbons. No attempt has been made to include references to purely pyrolytic investigations, or to catalytic processes, since a number of comprehensive reviews of this kind already exist (35, 36, 41, 42, 43, 45, 46, 48, 57, 77, 181, and especially 40). In spite of their importance, the oxidation and halogenation reactions of the hydrocarbons have not been included, since these do not seem to have advanced as yet to the stage where we can disentangle the processes into their component parts with any degree of certainty. In any case these subjects have been frequently reviewed (44, 47, 117, 132, 183).

Inasmuch as the available information regarding the reactions of the simple hydrocarbons comes from a variety of sources, it will be advantageous to give a brief discussion of a number of points in a general way before embarking on a detailed analysis of the reactions of specific substances.

A. The kinetics of decomposition reactions

Since the discovery by Hinshelwood (73) in 1926 that a number of organic compounds decomposed by a first-order mechanism, the number of known first-order reactions has increased very rapidly, and it now appears that at least the primary step in almost all organic decomposition reactions is a unimolecular change. The whole question of the stability of gaseous organic substances is therefore virtually reduced to a consideration of the magnitude of the unimolecular velocity constant. This is usually expressed over a range of temperature in terms of the integrated form of the Arrhenius equation, i.e.,

$$k = Ae^{-E/RT}$$

or (A)

$$\log_{10} k = \log_{10} A - \frac{E}{2.3\,RT}$$

where A is a constant and E is the so-called energy of activation.

The modern theory of unimolecular reactions is based on the idea that activation is by collision, but that a time lag exists between activation and reaction, most activated molecules being deactivated before they have a chance to react. As a result there exists a stationary concentration of activated molecules, which is calculable from the Maxwell–Boltzmann distribution, and the rate of reaction is proportional to the first power of the concentration of the reacting substance. At low pressures, however, the diminished number of collisions will no longer be able to replace the activated molecules as fast as they are destroyed by reaction, their stationary concentration will fall, and hence the rate of reaction will diminish with decreasing pressure.

Thus, formally, we can represent the process by:

(1) $2A \rightarrow A + A^*$ activation by collision
(2) $A + A^* \rightarrow 2A$ deactivation by collision
(3) $A^* \rightarrow$ products reaction
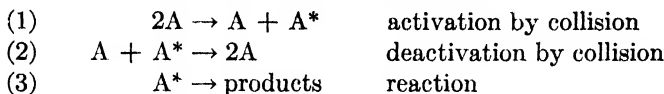
In the steady state

$$-\frac{d}{dt}[A^*] = +\frac{d}{dt}[A^*]$$

or

$$2k_1[A]^2 - k_3[A^*] - k_2[A][A^*] = 0$$

Whence

$$[A^*] = \frac{2k_1[A]^2}{k_3 + k_2[A]}$$

Now the overall rate of reaction is the rate of reaction 3, i.e., $k_3[A^*]$, hence

$$-\frac{d}{dt}[A] = \frac{2k_3 k_1[A]^2}{k_3 + k_2[A]}$$

At high pressures $k_2[A] \gg k_3$ and this reduces to

$$-\frac{d}{dt}[A] = \frac{2k_3 k_1[A]}{k_2}$$

i.e., the reaction is of the first order. At sufficiently low pressures, however, deactivation becomes slower on account of the diminished number of collisions, and eventually we have $k_3 \gg k_2[A]$. The rate expression then becomes

$$-\frac{d}{dt}[A] = 2k_1[A]^2$$

and the reaction becomes of the second order.   In the intermediate range the rate constant will fall with diminishing pressure and the reaction will have an order between 1 and 2.

The theory of unimolecular reactions is mainly concerned with the interpretation of the rate-pressure curve in the region where the velocity constants begin to fall below their high-pressure value.   In the development of such a theory it is necessary to be more specific concerning the nature of the energy of activation.   One type of theory assumes (72) that if a molecule has an energy $\geq E$ it has a definite probability of reacting, independent of its excess energy over and above E.   This is the simplest form of theory, but it gives a rate-pressure relationship which is definitely in disagreement with the facts.   The other type of theory assumes that for reaction energy must be concentrated in one particular degree of freedom, or in one vibrational bond of the molecule (82, 83, 167, 168, 169).   On this basis it is obvious that the chance of getting energy equal to or greater than E into one bond will be a function of the total energy of the molecule, and will increase rapidly with the excess of the energy of the molecule over E. This type of theory gives results which are in excellent agreement with the facts.   There are a number of different forms of the theory, but all are essentially the same.   That of Kassel (84) is much the simplest and is the one which is usually employed.

Kassel assumes that if a molecule has j quanta divided among s oscillators, it will react when m quanta are localized in a particular bond.   He then gets directly for the rate of reaction at high pressures

$$k_\infty = A(1 - e^{-h\nu/kT})^s \sum_{j=m}^{\infty} \binom{j+s-1}{s-1} \frac{j!(j-m+s-1)!e^{-jh\nu/kT}}{(j-m)!(j+s-1)!}$$

which on carrying out the summation reduces to

$$k_\infty = Ae^{-mh\nu/kT} \qquad \text{(B)}$$

Here A has the general character of the reciprocal of a relaxation time, i.e., it is a measure of the frequency with which the energy of the molecule is redistributed among the various oscillators, ν is the frequency of the oscillators all of which are for simplicity assumed to be identical, and k is the Boltzmann constant.   It is not necessary for us to discuss here the situation at low pressures, where the rate has "fallen off" from its high-pressure value.

A comparison of equations A and B shows that

$$mh\nu = E/N_0$$

where N_0 is Avogadro's number.   In other words, the activation energy is merely the total energy of that number of quanta which must be located in the pertinent bond before reaction can occur.

Obviously, for the purpose of predicting the products of decomposition reactions, it becomes a matter of major importance to discover any possible correlation between the activation energy of a reaction and the strengths of the bonds formed and broken in it. This question is discussed in the following section.

B. Free radicals in organic decomposition reactions

There is at present considerable uncertainty concerning the manner in which a large number of organic compounds decompose at high temperatures. Consider, for example, the decomposition of gaseous acetaldehyde to yield methane and carbon monoxide. There are two main mechanisms by which this process might occur:

(1) *The molecular mechanism:* In this case acetaldehyde splits into its final stable decomposition products in a single step,

$$CH_3CHO \rightarrow CH_4 + CO$$
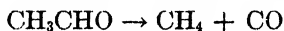
This involves the simultaneous rupture of two valence bonds and the formation of one new one. It is obvious, therefore, that the activation energy of the process will bear no simple relation to the bond strengths.

(2) *The free-radical mechanism:* It is, however, possible that the primary step consists of the rupture of only a single bond, giving rise to two unsaturated radicals,

$$CH_3CHO \rightarrow CH_3 + CHO$$
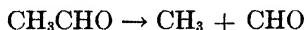
and that these radicals undergo secondary reactions which ultimately lead to the formation of methane and carbon monoxide. If this mechanism is the true one, and if the later reactions are fast compared with the primary step, the activation energy will be a direct measure of the strength of the only bond broken in the primary step, the C—C bond.

Rice (166) has suggested that virtually all organic compounds decompose by such a free-radical mechanism. If such a theory is to stand, it is obviously necessary to show in the first instance that free radicals are capable of existence. This had already been accomplished by Paneth and Hofeditz (134), who showed that free methyl radicals from the decomposition of organic compounds could be detected in a rapidly flowing gas stream by their reaction with a lead mirror to form volatile organometallic compounds. Following this discovery, Rice and his coworkers (156 to 166) made a comprehensive investigation of organic decomposition reactions from this point of view. They found that free radicals could be detected in the decomposition of almost all gaseous organic substances.

On account of the low pressures, fast flow, etc., which must be used in such experiments, it is necessary to work at temperatures which are from 200° to 300°C. higher than those at which the ordinary thermal decom-

position sets in. Hence, while it is certain that radicals are present at very high temperatures, such tests do not *prove* their presence during ordinary thermal decomposition at lower temperatures.

The theory has met with its greatest success in predicting the products of organic decomposition reactions (159), especially those of the hydrocarbons. The observed activation energies of the decomposition reactions of most organic substances lie between 35 and 70 kg-cal. Rice points out that if two reactions have activation energies different by 4 kg-cal., then the relative rates at 600°C. are in the ratio $e^{-4000/2 \times 873}$ to 1, or approximately 9 to 1. Similarly for a difference of 10 kg-cal. the rates will be in the ratio of 500 to 1. It follows, therefore, that if there are two or more possible modes of decomposition of a compound, then if one of these has an activation energy 10 kg-cal. or more lower than that of any of the others, it alone will occur to an appreciable extent. (This argument is usually correct. It has exceptions however, since in some cases the variation in A in equation A (page 312) is sufficient to counterbalance a difference in E. In most cases, however, the values of A are the same to within one power of 10 and equal to about 10^{13}.)

There is still some uncertainty about the values of the strengths of the C—C, C—H, C=C, and C≡C bonds. It is, however, certain that the C≡C and C=C bonds are very much stronger than the others, and it appears probable that the C—H bond is about 15 kg-cal. stronger than the C—C bond (204). We may therefore conclude that if the decomposition of a hydrocarbon occurs through free radicals it will always split at a C—C bond, and never at a C—H or a double or triple bond.

Thus in the case of propane, for example, the primary reaction can only be

$$C_3H_8 \rightarrow CH_3 + C_2H_5$$

Now methyl and ethyl radicals can be detected by the Paneth technique, but normally not other higher radicals, presumably because when formed they decompose very rapidly into unsaturated compounds and CH_3, C_2H_5, or H. Some energy of activation will, in general, be required for each step, but this will usually be much smaller than that required for the primary split. In the case of propane we thus have the following scheme, R denoting a methyl radical or a hydrogen atom,

$$CH_3CH_2CH_3 \rightarrow CH_3 + CH_3CH_2 \tag{1}$$

$$CH_3CH_2CH_3 + R \rightarrow RH + CH_3CH_2CH_2 \tag{2a}$$

$$CH_3CH_2CH_2 \rightarrow C_2H_4 + CH_3 \tag{2b}$$

$$CH_3CH_2CH_3 + R \rightarrow RH + CH_3CHCH_3 \tag{3a}$$

$$CH_3CHCH_3 \rightarrow CH_3CH{=}CH_2 + H \tag{3b}$$
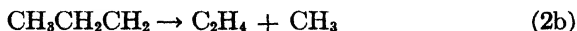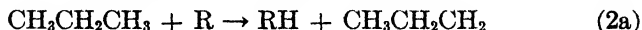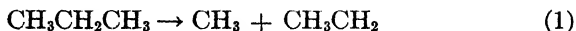
On the basis of chance we would expect reaction 2 to be faster than reaction 3 in the ratio of 3 to 1, since there are six primary hydrogen atoms to two secondary. There is, however, some evidence that secondary hydrogen atoms are somewhat less strongly bound. On this basis Rice estimates that reaction 2:reaction 3::6:4. Hence, neglecting all but the chain-carrying steps, we have for the overall decomposition

$$6C_3H_8 \rightarrow 6C_2H_4 + 6CH_4$$

$$4C_3H_8 \rightarrow 4C_3H_6 + 4H_2$$

$$\overline{10C_3H_8 \rightarrow 6C_2H_4 + 6CH_4 + 4C_3H_6 + 4H_2}$$
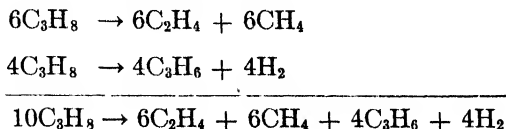
In general, this method gives rather good agreement with experiment, and the results will be discussed later for specific cases.

If the free-radical theory of organic decomposition reactions is to be accepted, however, it must account not only for the products of organic decompositions, but also for the kinetics of such processes. It is an experimental fact that almost all organic decomposition reactions are of the first order, and it is therefore necessary for the theory to answer two questions: (a) If the measured process is really the summation of a complex series of reaction steps, how is it that the overall reaction appears to be of the first order? (b) If, as is postulated, most reactions occur by the breaking of a C—C bond, how is it that experimental activation energies for decomposition reactions are usually far smaller than the strength of this bond?

Rice and Herzfeld (162) answered these questions by showing that mechanisms could be devised on a free-radical basis which would lead to a first-order overall rate. Further, by a suitable choice of the activation energies of the part reactions, the apparent activation energy of the overall reaction could be made to agree perfectly with the experimental value. As an example, consider the following scheme for the decomposition of an organic molecule M_1 (166):

<div align="center">E in kg-cal.</div>

$$M_1 \rightarrow R_1 + M_2 \qquad 80 \qquad (1)$$

$$R_1 + M_1 \rightarrow R_1H + R_2 \qquad 15 \qquad (2)$$

$$R_2 \rightarrow R_1 + M_3 \qquad 38 \qquad (3)$$

$$R_1 + R_2 \rightarrow M_4 \qquad 8 \qquad (4)$$
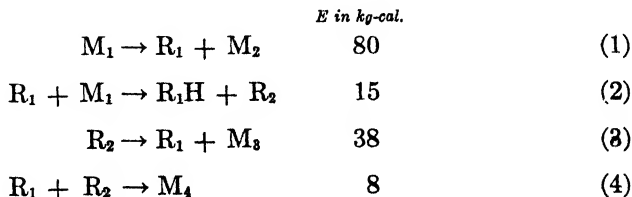
The molecule M_1 is assumed to decompose into a radical R_1 and a molecule M_2. The radical R_1 reacts with a fresh molecule of the reactant, abstracts a hydrogen atom, and forms the stable substance R_1H and the radical R_2. R_2 then decomposes into the radical R_1 and a molecule M_3.

We thus have a chain process, since steps 2 and 3 can repeat over and over again. The chain is finally broken when the radicals combine to form a stable molecule by reaction 4.

If we set up the equations giving the concentrations of the radicals in the steady state, we have, assuming long chains,

$$\frac{d}{dt}[R_1] = 0 = k_1[M_1] - k_2[R_1][M_1] + k_3[R_2] - k_4[R_1][R_2] \tag{5}$$

$$\frac{d}{dt}[R_2] = 0 = k_2[R_1][M_1] - k_3[R_2] - k_4[R_1][R_2] \tag{6}$$

Now the overall rate of decomposition of M_1 is given by

$$-\frac{d}{dt}[M_1] = k_1[M_1] + k_2[R_1][M_1] \tag{7}$$

If we solve equations 5 and 6 for R_1 and substitute the result in equation 7, we get

$$-\frac{d}{dt}[M_1] = k_1[M_1](1 + \sqrt{k_2 k_3/2k_1 k_4}) \sim [M_1]\sqrt{\frac{k_2 k_3 k_1}{2k_4}}$$

i.e., the reaction is of the first order. Furthermore

$$E_{\text{overall}} = 1/2\,(E_1 + E_2 + E_3 - E_4)$$

so that, using the values of E for the part reactions given above, we get

$$E_{\text{overall}} = 62.5 \text{ kg-cal.}$$

which is much below the strength of the C—C bond.

It should be emphasized at this point that the prediction of a first-order overall rate is dependent on the assumption made regarding the method of termination of the reaction chains. The above scheme assumes that they end by radical recombination

$$R_1 + R_2 \rightarrow M_4$$

and, as we have seen, this leads to a first-order rate. If, however, we were to assume as the chain-terminating reaction

$$2R_1 \rightarrow M_5$$
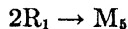
the overall order would be 3/2, while

$$2R_2 \rightarrow M_6$$
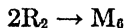
would give 1/2. The successful prediction of a first-order rate therefore depends on the arbitrary assumption that the reaction

$$R_1 + R_2 \rightarrow M_4$$

is much faster than the other two possible radical recombination reactions. As we shall see later, this leads to serious difficulties in the application of the scheme to specific reactions.

Mechanisms of this sort are, of course, highly speculative. Striking support for the fundamental idea of free-radical chain reactions was, however, immediately forthcoming. Frey (57) was able to start chains in butane at temperatures below its normal decomposition range by adding methyl radicals (from the decomposition of dimethyl mercury). Similarly, Allen and Sickman (1, 184) showed that chain decomposition of acetaldehyde could be caused by methyl radicals from the decomposition of azomethane. Leermakers (105) also produced sensitized chain decomposition of methyl ether at temperatures below 400°C. by photolyzing admixed acetone. All these observations prove that radicals *can* cause chain decomposition of a large number of organic substances. They do not, however, necessarily prove that such free-radical chain decomposition occurs in the normal pyrolysis of the substances concerned.

Further evidence for the chain character of a number of decomposition reactions is furnished by the work of Staveley and Hinshelwood (188b, 189, 190) and others (39, 55, 126, 194). They found that while large amounts of added nitric oxide would catalyze the reactions, small amounts caused some inhibition. They assume that the maximum inhibition corresponds to the complete suppression of chains normally present, and thus calculate chain lengths of from two to fifteen for a number of decomposition reactions. This is definite evidence for the presence of chains, but in most cases the chain lengths thus obtained are far too small to be in accord with the Rice–Herzfeld mechanisms. However, the assumption that maximum inhibition corresponds to a complete suppression of all chains is arbitrary, and makes the calculated chain lengths of somewhat doubtful significance. Recent work on some reactions (191, 191a) indicates that in certain cases there may be a few long chains rather than a large number of short ones, i.e., that the Rice–Herzfeld mechanisms may hold for a small fraction of the total reaction, the remainder of the substance decomposing by a molecular mechanism.

It may therefore be concluded that, on the whole, the evidence of a general nature favors the free-radical theory. However, when the specific Rice–Herzfeld mechanisms for a number of reactions are tested the situation is quite different. Up to the present three methods have been used for this purpose: (*a*) The stationary hydrogen-atom concentration during a decomposition reaction is measured and compared with the value calculated from the theory (135, 136, 137, 138, 174, 175). (*b*) The activation energy of one of the part reactions in the Rice–Herzfeld scheme is determined in an independent way (196, 226). (*c*) Deutero-compounds are

used as indicators of the mechanism (193). All these methods seem to indicate that the Rice-Herzfeld mechanisms are untenable.

The status of the free-radical theory of decomposition reactions thus seems at the moment to be an open question. In a general way the theory serves to correlate an enormous number of facts, and it has pointed the way to a great deal of fruitful work. When examined closely, however, it seems to fail in almost every case. The most reasonable conclusion seems to be that the theory is in part correct, but that its present form is incomplete and too broad. We shall examine the evidence for and against its applicability in specific cases in later sections.

Numerous other suggestions have been made to explain how a molecule may split so as to give rise to several different products. Thus it has been suggested (85) that the decomposition of a paraffin might proceed by

$$RCH_2CH_3 \rightarrow RH + CH_3CH=$$

$$CH_3CH= \rightarrow CH_2=CH_2$$
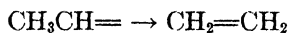
i.e., an initial split to give an alkylidene radical which rearranges practically instantaneously to an olefin. In this case, if the second reaction were fast enough, the process would be indistinguishable from a direct split into stable molecules.

C. Photochemical and atomic reactions

From the foregoing discussion it follows that a knowledge of the "elementary" reactions of the hydrocarbons is of special importance in any attempt to unravel the kinetics of their thermal reactions. Independent methods of obtaining information concerning the reactions of radicals will thus be of the greatest importance. Information of this sort may often be obtained from photochemical investigations. Indeed the reactions of atoms and radicals really constitute the connecting link between thermal and photochemical kinetics. The activation mechanism is, of course, quite different in the two types of reaction, involving activation by collision in the one case, and absorption by the chromophoric group in the other. However, once the primary step has occurred, the subsequent stages of a photochemical process are thermal reactions, and these often involve atoms and radicals.

In the following sections, therefore, we shall discuss the photodecomposition of the hydrocarbons. Unfortunately very little information is available, since the simple hydrocarbons are transparent down to the extreme ultra-violet, and the difficulties involved in working in the Schumann region have deterred most investigators. Most of the photochemical

work has, on this account, been done by photosensitization with mercury vapor. In work of this sort mercury vapor is mixed with the reactant gas and the mixture is illuminated with the mercury resonance line at 2537 A.U. This is absorbed by the mercury vapor in the system, normal mercury atoms being raised to the 2^3P_1 level. This lies 4.8 volts or 112 kg-cal. above the ground state. Such excited mercury atoms may then transfer their energy by collision to other molecules. If such transfer takes place efficiently, a wide variety of reactions is possible (28, 209, 213, 214, 216), since 112 kg-cal. is greater than the activation energy of almost all chemical reactions.

The mercury photosensitization method is especially important, since Taylor and his coworkers have shown that it allows us to investigate reactions involving hydrogen atoms. In the presence of hydrogen and a reacting substance we have

$$Hg(1^1S_0) + h\nu \rightarrow Hg(2^3P_1) \tag{1}$$

$$Hg(2^3P_1) + H_2 \rightarrow Hg(1^1S_0) + 2H \tag{2}^1$$

$$H + X \rightarrow products \tag{3}$$

$$2H + (a\ third\ body) \rightarrow H_2 \tag{4}$$
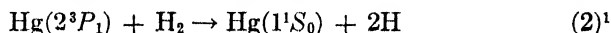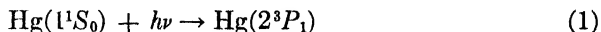
Under these circumstances a stationary concentration of hydrogen atoms exists, and, knowing the rates of reactions 1, 2, and 4, we can calculate the velocity constant of reaction 3 (2, 52, 186). The method is of wide applicability, although the results are not always easy to interpret.

The reactions of hydrogen atoms can also be investigated in a much more direct way, although not under as wide a variety of experimental conditions, by the Wood–Bonhoeffer method. It was first shown by Wood (236) that it was possible under certain circumstances to pump hydrogen atoms out of a hydrogen discharge tube in large quantities, and to carry them for considerable distances before recombination occurred. The method was adapted to the investigation of hydrogen atom reactions by Bonhoeffer (20, 21), and a large number of reactions have been investigated in this way (61).

We shall now proceed to a detailed examination of the available kinetic data for each of the simple hydrocarbons.

[1] Recent work (13, 172) makes it appear probable that reaction 2 should be

$$Hg(2^3P_1) + H_2 \rightarrow HgH + H$$
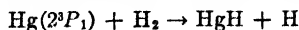
This introduces a numerical change into calculations of the hydrogen-atom concentration, but does not affect general considerations about the process.

II. THE PARAFFINS

A. Methane

1. The thermal decomposition

A very thorough discussion of the older work, of pyrolytic investigations, and of investigations of the equilibrium

$$CH_4 \rightleftarrows C + 2H_2$$

has been given by Egloff (40).

The first investigations of much kinetic importance were made by Holliday and his coworkers. Holliday and Exell (75) investigated the decomposition of methane in silica bulbs at temperatures from 800° to 1100°C. They found that the first 60 per cent of the methane present decomposed regularly, and that a "false equilibrium" was then reached which had no relation to the true equilibrium

$$2CH_4 \rightleftarrows C_2H_2 + 3H_2$$

They found that hydrogen had a pronounced retarding effect upon the reaction, so that their false equilibrium was presumably merely a pronounced slowing down of the reaction by the hydrogen formed in it. This phenomenon had been previously noted by Cantelo (27). The reaction was not sensitive to the condition of the surface, inasmuch as the same general results were obtained in clean and in carbon-coated silica bulbs and in porcelain. Holliday and Gooderham (76) made exhaustive tests of the homogeneity of the reaction. They assumed that the initial step was

$$2CH_4 \rightarrow C_2H_2 + 3H_2 - 91,000 \text{ cal.}$$
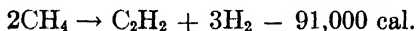
As Kassel has pointed out (86), their arguments in favor of this mechanism seem to be quite irrelevant. There is little in favor of it, and it is ruled out in any case, since it would require the activation energy of the reaction to be greater than 91,000 cal.; this is contrary to the facts.

In a thorough investigation Kassel found the reaction to be homogeneous and of the first order at from 1.3 to 29.6 cm. initial pressure, and he confirmed the strong retardation by hydrogen. According to his measurements the initial rate can be expressed by

$$k = 1.0 \times 10^{12} \, e^{-79,385/RT} \text{ sec.}^{-1}$$

with an uncertainty in the activation energy of perhaps 6000 cal. The rate in the later stages of the reaction was found to be approximately proportional to the square of the methane concentration and inversely

proportional to the cube of the hydrogen concentration. He suggests as possible initial steps (the numbering is his):

$$CH_4 \rightarrow CH_3 + H - 125,000 \text{ cal.} \tag{2}$$

$$CH_4 \rightarrow CH_2 + H_2 - 47,000 \text{ cal.} \tag{3}$$
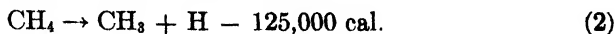
The experimental value of E strongly favors reaction 3 as the primary step. In the early stages of the reaction the only possible reaction of the methylene radical is

$$CH_2 + CH_4 \rightarrow C_2H_6 + 36,000 \text{ cal.} \tag{4}$$
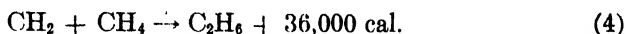
and at these high temperatures ethane will decompose rapidly

$$C_2H_6 \rightarrow C_2H_4 + H_2 - 30,000 \text{ cal.} \tag{5}$$
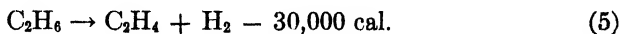
At the low partial pressures of ethylene which would prevail here polymerization would not be important, so that as possible reactions of ethylene we have

$$C_2H_4 \rightarrow C_2H_2 + H_2 - 48,000 \text{ cal.} \tag{6}$$

$$C_2H_4 \rightarrow 2CH_2 \qquad - 53,000 \text{ cal.} \tag{7}$$

$$C_2H_4 + CH_4 \rightarrow C_3H_8 \qquad + 17,000 \text{ cal.} \tag{8}$$
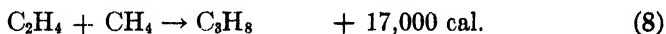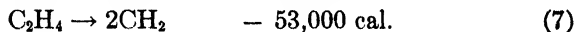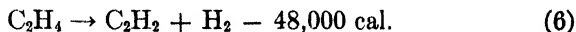
Reaction 6 is probably the only one of these which is important. Acetylene may also be assumed to dissociate as follows:

$$C_2H_2 \rightarrow 2C + H_2 \tag{12}$$

Using this scheme we get for the initial stages of the reaction approximately

$$-\frac{d}{dt}[CH_4] = 2k_3[CH_4]$$

i.e., the reaction is of the first order. After a certain amount of hydrogen has accumulated we get

$$-\frac{d}{dt}[CH_4] = \frac{2k_3 k_4 k_5 k_6 k_{12}[CH_4]^2}{r_3 r_4 r_5 r_6 [H_2]^3}$$

where the r's signify the velocity constants of the reverse reactions.

The above equation is in excellent agreement with Kassel's results. In support of this mechanism Storch (199) showed that the earliest product which could be detected was ethane. This was done by decomposing methane on a carbon filament at low pressures in a bulb cooled in liquid nitrogen. Storch (200) has also discussed in detail the results of a number

of investigators who used flow methods to investigate the pyrolysis of methane. Where necessary he makes reasonable assumptions about dimensions of reaction vessels, etc., in order to calculate velocity constants from their data. He concludes that Kassel's mechanism fits the data to within a factor of 2, which is all that can be expected considering uncertainties in temperature, etc. The experiments thus considered were as follows:

AUTHORS	TEMPERATURE RANGE IN °C.
Rudder and Biedermann (173) . .	900–1500
Wheeler and Wood (234) ..	1050
Stanley and Nash (188) ..	1100–1150
Smith, Grandone, and Rall (187) .	1200
Fischer and Pichler (53) .. .	1260–1600
Storch and Golden (203) . ..	1500

For a discussion of the sources of error in these measurements, etc., Storch's paper should be consulted.

The velocity constants referred to above are, of course, for the total conversion of methane. Storch also concludes that the conversion of methane to $(C_2H_2 + C_2H_4)$ can be formally represented as a unimolecular reaction with an activation energy of 64,000 cal., i.e.,

(per cent conversion to C_2H_x) (partial pressure of CH_4) = constant

at any temperature. Whatever the explanation of this result may be, combining Storch's equation with that of Kassel enables one to predict the rate of formation of any given product over the whole temperature range.

The decomposition of methane at very high temperatures has been investigated by Tropsch and Egloff (227).

2. Free radicals and the decomposition of methane

Rice and Dooley (158, 161) investigated the primary process in the decomposition of methane by the free-radical technique. Using tellurium mirrors, they found that $CH_3Te \cdot TeCH_3$ was formed and not $(CH_2Te)_n$, and so concluded that the primary process involved methyl rather than methylene radicals. The activation energy of the split into free radicals was found to be 100 ± 6 kg-cal. Belchetz and Rideal (7, 8) passed methane rapidly over a hot filament at low pressures, and then onto a cold target about one mean free path away. Radicals were detected by their

reactions with mirrors, iodine, etc. Contrary to the findings of Rice and Dooley, they conclude that the primary step is

$$CH_4 \rightarrow CH_2 + H_2$$

rather than

$$CH_4 \rightarrow CH_3 + H$$

They found no evidence of the presence of methyl radicals, although this, of course, does not preclude their appearance under other experimental conditions. They point out that metallic methyl compounds may be easily formed by reduction, and hence Rice's technique might lead to false conclusions, since telluroformaldehyde is very easily reduced to dimethyl telluride. The activation energy of the split into methylene and hydrogen was found to be 95 kg-cal., in substantial agreement with the activation energy found by Rice and Dooley.

If we accept Rice and Dooley's detection of the methyl radical as valid, then, as they point out, there are two opposing mechanisms for its formation:

$$CH_4 \rightarrow CH_3 + H \qquad \left.\begin{array}{l}\text{Rice} \\ \text{and} \\ \text{Dooley}\end{array}\right\} \qquad \begin{array}{l}(1) \\ \\ (3)\end{array}$$

$$H + CH_4 \rightarrow H_2 + CH_3$$

$$CH_4 \rightarrow CH_2 + H_2 \qquad \left.\begin{array}{l}\text{Belchetz} \\ \text{and} \\ \text{Rideal}\end{array}\right\} \qquad \begin{array}{l}(2) \\ (4) \\ \\ (5)\end{array}$$

$$CH_2 + CH_4 \rightarrow 2CH_3$$

$$CH_2 + CH_4 \rightarrow C_2H_6$$
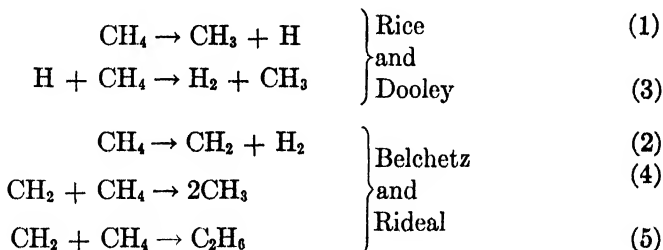
If reaction 2 is the correct primary step, rather than reaction 1, then either reaction 4 or reaction 5 must have an activation energy less than 12 kg-cal. to account for the absence of methylene radicals at the mirror in the experiments of Rice and Dooley. They consider this to be much too low, and hence they favor reaction 1 as the primary step. No hydrogen telluride is formed in their experiments, as would be the case if hydrogen atoms reached the tellurium mirror. They therefore conclude that hydrogen atoms must disappear from the system rapidly by wall recombination or by reaction 3.

Assuming a chain reaction due to methyl radicals as postulated above, Kassel (88) has shown that it would be necessary for [H] to be 10^4 times greater than [CH_3]. It does not seem possible that such a factor could be overcome by wall recombination of hydrogen atoms to such an extent that they do not reach the mirror in appreciable quantities. Hence Kassel rules out reaction 1 as the initial step. Further, since the methylene

radical was not identified by the Rice technique in the diazomethane decomposition, there is no reason to expect it to be found here even if the primary step is reaction 2. He concludes that reaction 5 is probably fast enough to keep the concentration of methylene radicals down to a very low value.

In connection with the discussion of the mechanism of the primary reaction, it may be noted that Mecke (121, 122) has suggested that the second hydrogen atom in methane may be much more weakly bound than the first.

Recent calculations by Voge, however, lead to the values (229a)

$$CH_4 \rightarrow CH_3 + H - 113,000 \text{ cal.}$$

$$CH_3 \rightarrow CH_2 + H - 94,000 \text{ cal.}$$

whence

$$CH_4 \rightarrow CH_2 + H_2 - 104,000 \text{ cal.}$$
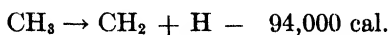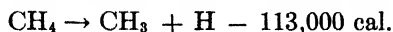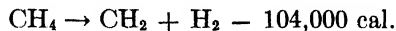
If we eliminate the zero-point energy correction so as to get chemical heats of reaction, and correct the results to bring them into line with a more recent and reliable estimate of the heat of sublimation of graphite (70a), Voge's values become .

$$CH_4 \rightarrow CH_3 + H - 99,000 \text{ cal.}$$

$$CH_3 \rightarrow CH_2 + H - 84,000 \text{ cal.}$$

$$CH_4 \rightarrow CH_2 + H_2 - 80,000 \text{ cal.}$$
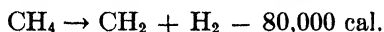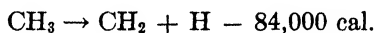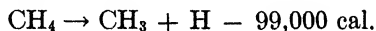
This would make the latter reaction just possible as the rate-determining step in the methane decomposition.

3. The photodecomposition of methane

Bonhoeffer (22) has discussed the photodecomposition of methane on the basis of the spectroscopic observations of Leifson (106) and Scheibe (177, 178, 179). Methane is transparent down to the Schumann region, and hence no photodecomposition can occur above this (214). Diffuse bands appear in the neighborhood of 1600 A.U., for which he suggests that the primary process is

$$CH_4 \rightarrow CH_3 + H$$

with the possible secondary reactions

$$2CH_3 \rightarrow C_2H_6 \qquad (a)$$

$$CH_3 + H \rightarrow CH_4 \qquad (b)$$

$$2H \rightarrow H_2 \qquad (c)$$

We would expect reaction b to be important, and hence the quantum yield to be low for the overall reaction

$$2CH_4 \rightarrow C_2H_6 + H_2$$
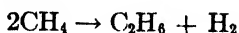
The results of two direct investigations of the photodecomposition have recently been described in brief notes. Leighton and Steiner (107) find that methane is decomposed by light from a hydrogen lamp near the limit of fluorite. Considerable hydrogen and unsaturated hydrocarbons are formed in the approximate mole ratio of 4 to 1, and the quantum yield is approximately unity. The formation of unsaturates can, of course, be easily accounted for if we assume

$$CH_4 + h\nu \rightarrow CH_2 + H_2$$

$$2CH_2 \rightarrow C_2H_4$$
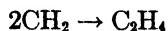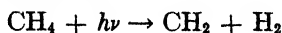
The high ratio of hydrogen to unsaturates, however, indicates that this cannot be the only process involved.

Groth and Laudenklos (66) used a Harteck xenon lamp as a source. This has strong lines at 1469 A.U. and 1295 A.U. They found that a 30-mm. layer of methane at a pressure of 1 atm. absorbed to the extent of 13 per cent at 1469 A.U. and completely at 1295 A.U. The products of the reaction were found to be mainly hydrogen and acetylene, with some ethane and traces of ethylene and C_3 to C_5 hydrocarbons. The quantum yield was 1.30 per mole of hydrogen formed. Their results are thus in excellent general agreement with those of Leighton and Steiner, and they suggest a somewhat similar mechanism, viz.,

$$CH_4 + h\nu \rightarrow CH_3 + H$$

$$CH_3 + H \rightarrow CH_2 + H_2$$

$$2CH_2 \rightarrow C_2H_2 + H_2$$
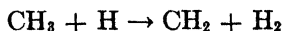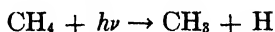
In any case it appears that Bonhoeffer's suggested mechanism is not valid.

In the past all observations indicated (90, 214, 219) that methane is stable in the presence of mercury atoms excited by resonance radiation, and hence that the mercury-photosensitized decomposition of methane could not be investigated. Recently, however, Morikawa, Benedict, and Taylor (129) have shown that the reaction

$$Hg^* + CH_4 \rightarrow CH_3 + H + Hg$$

has a low activation energy. This question is discussed in detail in the following section.

In an electrical discharge methane is decomposed into a variety of

products. Spectroscopic examination of the discharge shows (150) that at least a part of the methane undergoes all the possible dehydrogenation steps, yielding CH_3, CH_2, CH, and C. These then recombine in various ways to give a variety of products.

4. The reaction of hydrogen atoms with methane

The reactions of various hydrocarbons with hydrogen atoms were investigated by Bonhoeffer and Harteck (23). They pointed out that since from an energetic standpoint both C—C and C—H bonds can be broken in a hydrogen atom reaction (except, of course, in the case of methane), we have in general three possibilities:

(a) *Dehydrogenation*, e.g.,

$$C_2H_6 + H \rightarrow C_2H_5 + H_2$$
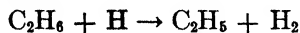
(b) *Chain breaking*, e.g.,

$$C_2H_6 + H \rightarrow CH_4 + CH_3$$
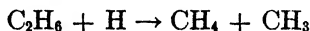
(c) *Hydrogenation*, e.g.,

$$CH_3 + H \rightarrow CH_4$$

Reaction c may occur at the wall or by dreierstoss, and in the case of complex radicals it can probably occur also in two-body collisions, the multiplicity of energy levels removing the dreierstoss restriction. If reactions a and c occur simultaneously, we may have nothing more than a "catalytic" recombination of hydrogen atoms. Bonhoeffer and Harteck found that methane was surprisingly stable, and they could detect no reaction with hydrogen atoms produced by the discharge tube method, although it might have been expected that the reaction

$$H + CH_4 \rightarrow CH_3 + H_2$$
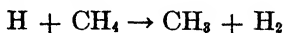
would occur.

These results were confirmed by von Wartenberg and Schultze (231). They also found that no appreciable heat was developed on mixing hydrogen atoms and methane (apart from the normal amount due to the recombination of the atoms). Further confirmation of the inertness of methane was furnished by the work of Chadwell and Titani (29).

Geib and Harteck investigated the process over a range of temperatures and showed that no reaction occurred up to 183°C. (63). They therefore concluded that the reaction

$$CH_4 + H \rightarrow CH_3 + H_2$$
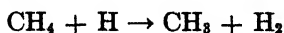
has an activation energy of at least 17 kg-cal. It might be suggested that this reaction really occurs readily, but that the back reaction

$$CH_3 + H + M \rightarrow CH_4 + M$$

proceeds more rapidly than other possible reactions of the methyl radical such as

$$2CH_3 \rightarrow C_2H_6$$
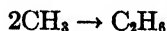
so that methane is reformed as fast as it is used up. Geib and Harteck ruled out such a suggestion on the grounds that (a) it is exceedingly unlikely that no other secondary reactions of the methyl radical should occur, and (b) the presence of methane causes no appreciable alteration in the hydrogen-atom concentration, whereas the above mechanism would involve the consumption of hydrogen atoms by both the forward and the reverse reactions.

This second objection could be overcome, however, by assuming the secondary reaction to be

$$CH_3 + H_2 \rightarrow CH_4 + H$$
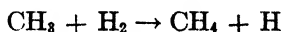
and thus regenerating the hydrogen atoms lost in the primary step. The activation energy of this reaction has been estimated to be about 8 kg-cal. by von Hartel and Polanyi (230). They investigated the reaction of sodium vapor with methyl chloride, using hydrogen as a carrier gas for the sodium. A certain amount of methane is formed under these conditions, presumably by

$$Na + CH_3Cl \rightarrow NaCl + CH_3$$

$$CH_3 + H_2 \rightarrow CH_4 + H$$
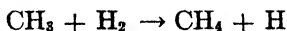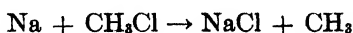
By using the hydrogen consumption as a measure of the latter step, they estimated its activation energy. The result is not very certain, however, since they were not really very sure of the exact mechanism of the formation of methane, and there is also a possibility of an alteration in the concentration of methyl radicals with increased temperature, owing to other secondary reactions. Further information about this reaction was obtained by Sickman and Rice (185). In an investigation of the effect of foreign gases on the azomethane decomposition they found that hydrogen is not an "inert gas," while deuterium is. They conclude that this is due to the occurrence of the processes

$$CH_3 + H_2 \rightarrow CH_4 + H \tag{1}$$

$$H + \text{azomethane} \rightarrow \text{products} \tag{2}$$
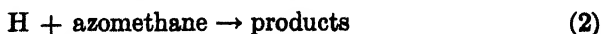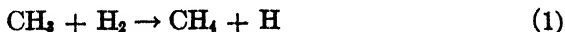
Either process 1 or process 2 must be slower for deuterium than for hydrogen, presumably process 1, since there would be no zero-point energy difference for process 2 other than that of the activated complex. Their results indicate, then, that reaction 1 is appreciable around 300°C. On the other hand Leermakers (104) concluded that the companion reaction

$$C_2H_5 + H_2 \rightarrow C_2H_6 + H$$
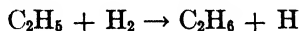
was not detectable at 275°C., indicating an activation energy greater than 15 kg-cal. There is thus considerable uncertainty about reaction 1, but it seems to be the consensus of opinion that von Hartel and Polanyi's estimate of the activation energy is much too low. Patat (135) investigated the concentration of methyl radicals and hydrogen atoms present during the photodecomposition of acetaldehyde. He found that in order to get agreement with von Hartel and Polanyi's experimental value of the activation energy of reaction 1 it was necessary to assume the very unlikely value of 10^{-4} for the steric factor. If the steric factor is taken as unity, a value of 20 kg-cal. is obtained for the activation energy of the reaction. In order to get the best agreement with free-radical mechanisms, Rice (158) arbitrarily puts E_1 equal to 23 kg-cal. He points out that if von Hartel and Polanyi's estimate of 8 kg-cal. were correct, it should be impossible to get appreciable quantities of methyl radicals in the presence of hydrogen, while in fact it is possible to do so. However, it seems almost certain that Rice's estimate is too high. Paneth, Hofeditz, and Wunsch (134a) investigated the rate of recombination of methyl radicals, using both hydrogen and helium as carrier gases. They found that the loss of methyl radicals was more rapid in hydrogen than in helium, even at room temperature. Under these conditions methane is formed, and it appears certain that this is due to the occurrence of reaction 1. Their data indicate that the activation energy of the reaction is about 15 kg-cal.

In view of these uncertainties, it follows that Geib and Harteck's arguments are not entirely conclusive. As will be seen from the following discussion, however, the investigation of the reaction of deuterium atoms with methane proves conclusively that methane is not broken up and reformed, but is really inert to atomic hydrogen.

The first investigation of the deuterium atom reaction was made by Taylor, Morikawa, and Benedict (217), the atoms being produced by photosensitization with mercury, and the resulting deuteromethanes detected by infra-red spectroscopy. They reported considerable reaction from 40°C. to 300°C., and concluded that the activation energy of the process was very low, of the order of 5 kg-cal. The paper was only a preliminary note, and their more complete results, referred to later, do not confirm their previous conclusions.

Geib and Steacie (64, 65) investigated the same reaction by the Wood–Bonhoeffer method. They found no detectable reaction of deuterium atoms with methane up to 100°C., indicating that the activation energy of the exchange reaction is not less than 11 kg-cal., in contrast to the above results. Their investigation indicates that the reaction concerned is probably the analogue of the ortho–para hydrogen conversion, viz.,

$$CH_4 + D \rightarrow CH_3D + H \qquad (3)$$

rather than

$$CH_4 + D \rightarrow CH_3 + HD \qquad (4)$$
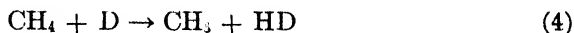
In any case a lower limit of 11 kg-cal. is set for both reactions. Subsequent work (192) furnishes further confirmation of the absence of a reaction between deuterium atoms produced by a discharge and methane at low temperatures.

A few preliminary experiments on the thermal exchange reaction between deuterium and methane at temperatures in the neighborhood of 1000°K. have been made by Farkas (50). His results show that the thermal reaction proceeds by an atomic mechanism, similar to the ortho–para hydrogen conversion, viz.,

$$D_2 \rightleftarrows 2D$$

$$D + CH_4 \rightarrow CH_3D + H$$
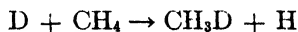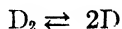
While the temperature coefficient of the reaction was not determined, an activation energy of about 11 to 12 kg-cal. was indicated.

The mercury-photosensitized reaction was reinvestigated at room temperature by Steacie and Phillips (196), who found an activation energy of 11.7 kg-cal. (assuming a steric factor of 0.1), in good agreement with the results of other methods. The reaction was also investigated by Farkas and Melville (51) over a wide range of temperature, and they found an activation energy of 13 kg-cal. In their investigation the atom concentration was determined by using ortho-deuterium-methane mixtures and measuring the rate of the ortho–para conversion as well as the exchange. They concluded, as did Steacie and Phillips, that the reaction occurring was reaction 3. They found, however, that at high temperatures the deuterium-atom concentration fell off greatly, and they suggest that the atom-consuming step is reaction 4. If this is the case, we would expect a small amount of ethane formation to accompany the exchange reaction.

In a recent paper Morikawa, Benedict, and Taylor (129) report a further investigation of the mercury-photosensitized reaction. From the collision yield at 100°C. they calculate for reaction 3 an activation energy of 12.5 to 14 kg-cal., in satisfactory agreement with the results of Steacie and

Phillips and of Farkas and Melville. The experimental value of the temperature coefficient in the range 100–200°C. is very low, however, and they conclude that the mechanism is not that postulated by these authors. They suggest that the reaction is largely

$$Hg^* + CH_4 \rightarrow CH_3 + H + Hg \qquad (E = 4.5 \text{ kg-cal.})$$
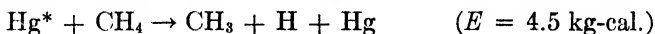
followed by a rapid exchange of the methyl radical, probably through the formation and decomposition of a quasi-molecule,

$$CH_3 + D \rightarrow CH_3D^* \rightarrow CH_2D + H$$

The fact that some ethane formation occurs is cited as evidence for this mechanism. They summarize the possible processes as:

(a) *Primary processes:*

$$Hg + h\nu \rightarrow Hg^*$$

$$Hg^* + D_2 \rightarrow Hg + 2D$$

$$Hg^* + CH_4 \rightarrow Hg + CH_3 + H$$

(b) *Secondary processes at low temperatures:*

$$D + D \rightarrow D_2 \qquad \text{(wall or third body)}$$

$$CH_3 + D \rightarrow CH_3D \qquad \text{(wall or third body)}$$

$$CH_3 + D \rightarrow CH_2D + H \qquad (E \leq 5 \text{ kg-cal})$$

$$CH_3 + CH_3 \rightarrow C_2H_6$$
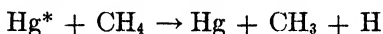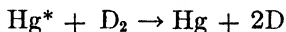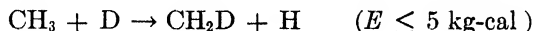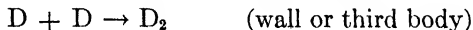
(c) *Secondary processes at higher temperatures:*

$$CH_3 + D_2 \rightarrow CH_3D + D \qquad (E = 11 \text{ kg-cal.})$$

$$CH_4 + D \rightarrow CH_3 + HD \qquad (E = 15 \text{ kg-cal.})$$

$$CH_3 + CD_4 \rightarrow CH_3D + CD_3 \qquad (E = 11 \text{ to } 15 \text{ kg-cal.})$$

together with later condensation and decomposition reactions. They discuss in detail the justification of these steps, and conclude that one cannot obtain much information about reaction 3 by the photosensitization method.

It seems to the writer, however, that the loss of hydrogen atoms at high temperatures found by Farkas and Melville is a sufficient explanation of the low temperature coefficient of the reaction, and that it is not necessary to postulate such a complicated series of processes. If one accepts this explanation, then the results of Morikawa, Benedict, and Taylor give an activation energy for the exchange reaction in good agreement

with the values of other investigators. It should be emphasized that the disagreement is primarily one of mechanism, not of experimental fact. There is, however, a considerable discrepancy in the quantum yields of the exchange reaction obtained by Farkas and Melville and by Morikawa, Benedict, and Taylor.

Further investigations of the reaction with deuterium atoms produced by the Wood–Bonhoeffer method have also been made by Trenner, Morikawa, and Taylor (226) and by Steacie (192). Steacie investigated the reaction up to 500°C. and obtained an activation energy of 12.9 ± 2 kg-cal., the values calculated from the temperature coefficient and from the collision yield being in good agreement.

Trenner, Morikawa, and Taylor by the same method found no reaction from 25°C. to 208°C., from which they calculate a minimum activation energy of 15.6 kg-cal. with a steric factor of 0.1. From a single run at 310°C. they calculate the activation energy to be 18 kg-cal. These values are higher than those obtained by other workers. The discrepancy is partly due to the fact that they assume that the process under investigation is reaction 4, followed by a rapid exchange of the methyl radical. Hence to get the rate of the initial step they divide the observed rate by 3. If we assume a direct exchange (i.e., reaction 3), this division by 3 should not be performed, and their activation energy would be lowered by about 1 kg-cal. They obtained the deuterium-atom concentration in their experiments by comparison with the reaction

$$H + D_2 \rightarrow HD + H$$
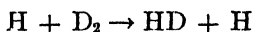
As far as one can tell from their paper, this comparison was made only at room temperature (although this is not certain). If this is the case their deuterium-atom concentration at higher temperatures would probably be somewhat lower than that assumed, and this would further lower the activation energy. It appears, therefore, that the discrepancy between their results and those of others is not large, and is mainly one of interpretation.

While there is thus some uncertainty about the exchange reaction, the main body of evidence favors an activation energy of about 12 to 13 kg-cal. for the reaction

$$CH_4 + D \rightarrow CH_3D + H$$
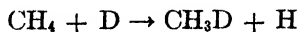
It may also be concluded that the reactions

$$CH_4 + D \rightarrow CH_3 + HD$$

and

$$CH_4 + H \rightarrow CH_3 + H_2$$
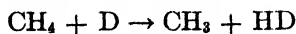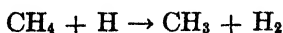
have activation energies greater than this.   In an excellent recent review of atomic reactions, Geib (61) points out that further evidence of the stability of methane to attack by hydrogen atoms is furnished by the fact that methane is obtained as an end product in many reactions of hydrogen atoms.

B. Ethane

1. The thermal decomposition

The first paper on the decomposition of ethane which contained any data other than purely pyrolytic was that of Pease (140).   He made a preliminary investigation of the reaction at 650°C. by the flow method and concluded that the reaction was homogeneous and probably of the first order, and that it went smoothly according to the equation

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

The addition of hydrogen was found to have no effect on the rate of the reaction or upon the products.   A brief investigation of the reaction by the static method at 575°C. by Frey and Smith (59) gave results in excellent agreement with those of Pease.   Neither of these investigations, however, was very detailed.

The first thorough investigation from a kinetic standpoint was that of Marek and McCluer (118), who used a flow method.   They concluded that the reaction was homogeneous and of the first order, the rate being given by

$$\log k = 15.12 - \frac{15,970}{T} \text{ sec.}^{-1}$$

after correcting for the reverse reaction.   This corresponds to an activation energy of 73,200 cal.   The main source of uncertainty in their work was the temperature of the reaction vessel, which was by no means uniform. Their value of the activation energy is therefore probably uncertain to ± 5000 cal.   Their results have been recalculated by Paul and Marek (139), who conclude that they are better expressed by the equation

$$\log_{10} k = 16.06 - \frac{77,700}{2.3RT} \text{ sec.}^{-1}$$

A more thorough investigation of the kinetics of the process was made by Sachsse (174), who used the static method and followed the reaction by the change in pressure.   He worked at temperatures from 856° to 910°K. and at pressures from 5 to 500 mm.   The velocity constants were found

to fall off with diminishing pressure in the customary way for a first-order reaction. His results for the high-pressure rates of reaction are given by

$$\log_{10} k = 14.1 - \frac{69,800}{2.3RT} \text{ sec.}^{-1}$$

He found that, in addition to ethylene and hydrogen, a certain amount of condensable products was formed, the amount increasing with the pressure.

The reaction has recently been reinvestigated by Storch and Kassel (203a). They find that in addition to the dehydrogenation reaction

$$C_2H_6 \rightarrow C_2H_4 + H_2$$
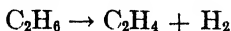
there is also methane and propylene production, which can be stoichiometrically represented by the equations

$$C_2H_6 \rightarrow CH_4 + \tfrac{1}{2} C_2H_4$$
$$C_2H_6 + C_2H_4 \rightarrow CH_4 + C_3H_6$$
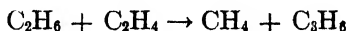
Butane may be an intermediate product for the latter reaction, but their experiments provide no direct test of this. However, Frey and Hepp (58a) showed that the analogous reactions

$$C_2H_4 + C_3H_8 \rightarrow C_5H_{12}$$
$$C_2H_4 + C_3H_8 \rightarrow CH_4 + C_4H_8$$
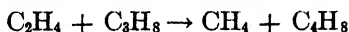
both occurred readily, the former being two to three times more frequent. Storch and Kassel therefore conclude that by analogy part of the methane and propylene found in their work is a product of the butane decomposition. They calculate their rate constants on this basis, using Paul and Marek's values for the rate of the butane decomposition. They thus obtain the values of the rate constants

$$(k_1) \qquad C_2H_6 \rightarrow CH_4 + \tfrac{1}{2} C_2H_4$$
$$(k_2) \qquad C_2H_6 + C_2H_4 \rightarrow C_4H_{10}$$
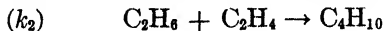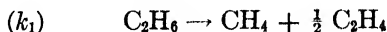
given in table 1A. For the initial rate of the dehydrogenation reaction

$$C_2H_6 \rightarrow C_2\dot{H}_4 + H_2$$

at 565°C. they thus obtained the velocity constants given in table 1B. Obviously the reaction is definitely of the first order. The agreement with Marek and McCluer's calculated velocity constant at 565°C., 11.6 × 10^{-5} sec.$^{-1}$, is not good. Paul and Marek's recalculation of Marek and McCluer's data gives 6.2 × 10^{-5} sec.$^{-1}$, in excellent agreement with Storch and Kassel's result. Sachsse's value, 10 × 10^{-5} sec.$^{-1}$ is not in very good agreement.

Dinzes, Zharkova, Zherko, and Frost (33c), who investigated the reaction at 635°C. and high pressures (1 to 26 atm.), also found that methane was produced. They suggested this was due to a concurrent reaction

$$2C_2H_6 \rightarrow 2CH_4 + C_2H_4$$

the influence of which increased with increasing pressure, as would be expected for a second-order reaction occurring simultaneously with one of the first order.

Since the rate of the reverse reaction

$$C_2H_4 + H_2 \rightarrow C_2H_6$$

has been measured by Pease (144), it is possible to calculate the equilibrium constant for the reaction and compare it with the experimental value.

TABLE 1A

Storch and Kassel's values of k_1 and k_2

TEMPERATURE	k_1	k_2
°C.	sec $^{-1}$	sec.$^{-1}$ mm.$^{-1}$
541	$2\ 62 \times 10^{-7}$	$1\ 85 \times 10^{-8}$
565	$1\ 00 \times 10^{-6}$	6.28×10^{-8}
600	6.14×10^{-6}	$3\ 31 \times 10^{-7}$
650	$6\ 44 \times 10^{-5}$	$2\ 83 \times 10^{-6}$

$E_1 = 75,400$ cal $\qquad E_2 = 69,000$ cal.

TABLE 1B

The dehydrogenation of ethane at 565°C (Storch and Kassel)

INITIAL PRESSURE	k	INITIAL PRESSURE	k
mm	sec $^{-1}$	mm	sec $^{-1}$
99.0	$9\ 2 \times 10^{-5}$	423 8	$5\ 5 \times 10^{-5}$
104 0	7.9	512 6	6 0
107 7	7 7	716 3	5 5
223 8	6 0	1093 4	5 6
224 1	6 0	1432 5	6 5
420 6	6 6	1517 0	6.9

Using Marek and McCluer's rates for the ethane decomposition, we thus get for the equilibrium

$$C_2H_4 + H_2 \rightleftarrows C_2H_6$$

$$\log_{10} K = 6.66 - \frac{30,020}{2.3RT}$$

The experimental value of Pease and Durgan (146) is

$$\log_{10} K = 6.31 - \frac{31,244}{2.3RT}$$

in excellent agreement with the calculated value. Had Sachsse's values for the ethane decomposition been used in the calculation, the result would have been much the same in the range covered by experiment, since his absolute rates are in fair agreement with those of Marek and McCluer in spite of the considerable difference in the temperature coefficient. Recent work by Storch and Kassel (203a) indicates that the situation is rather more complex. The question is discussed in detail in section III B.

The thermal decomposition has also been investigated by a static method by Dinzes and Frost (30, 31, 32). Their main object was to check accurately the unimolecular character of the reaction in the light of the Rice–Herzfeld chain theory. They followed the reaction by pressure change and by analysis at 678°C. and pressures from 1.7 to 22.3 mm. They found that the reaction did not follow the unimolecular equation well, the constants decreasing three or four times on going from 10 to 70 per cent decomposition. The course of an individual experiment could be expressed accurately by the equation

$$k = \frac{1}{t}\left(\log \frac{1}{1-x} - \beta x\right)$$

where x and t have the usual significance, and β is a constant. From the complex character of the rate equation they conclude that the reaction is probably a chain process. It seems certain, however, that at 678°C. the ethylene formed in the reaction would undergo a series of further complex changes, and one would hardly expect a first-order equation to hold up to high percentage decompositions under the circumstances. Dinzes, Kvyatkovskii, Stepukhovich, and Frost (33b) cite as further evidence for the complexity of the reaction that it is inhibited by the addition of propylene but not by ethylene or butylene.

The decomposition of ethane in sealed silica bulbs has also been investigated by Travers and his collaborators (222a, 223, 224, 225). They worked mainly with mixtures of ethane, ethylene, and hydrogen in order to eliminate the effect of the equilibrium, and thus study the formation of secondary products. Their results on the main decomposition process are very complex and are in complete disagreement with those of all other investigators. They conclude that there is a pronounced induction period, and that sharp breaks occur in curves representing the rate of formation of all the products concerned. They also find pronounced and complex surface effects, contrary to the findings of other workers. Travers (222, 222b) concludes that the whole process is governed by the "back-ground" reaction

$$C_2H_6 \rightleftarrows C_2H_4 + H_2$$

but that the rate-controlling step is the reaction

$$C_2H_6 + C_2H_4 \rightarrow (C_4H_{10}) \rightarrow CH_4 \text{ and condensation products}$$

It seems to the reviewer that little confidence can be placed in this work. The induction periods which they find are almost certainly due to the experimental technique, which consists of plunging a cold reaction vessel into a heated bath, and thus yields fictitious induction periods, which are really due to a lag in reaching temperature equilibrium. Further, the most striking thing about their results is the presence in every case of sharp breaks in curves representing the rate of formation of the various products. An examination of the analytical data, however, indicates that these breaks are also fictitious and are due to placing too much confidence in unchecked analytical results.

Fischer and Pichler (54) have investigated the decomposition of ethane at temperatures up to 1400°C. They find that the percentage conversion and the products are practically the same as those of ethylene at high temperatures. In other words, at high enough temperatures ethane dehydrogenates instantaneously to ethylene, which then pyrolyzes in the ordinary way.

2. The photodecomposition and the photosensitized decomposition

As Bonhoeffer has pointed out (22), all we can do in connection with the direct photodecomposition is to make speculations on the basis of rather meager spectroscopic information. The absorption is probably by the C—H bond, but possibly some of the energy wanders to the C—C bond. He suggests that the main process would probably be

$$C_2H_6 \rightarrow C_2H_5 + H$$

$$C_2H_5 + H \rightarrow C_2H_4 + H_2$$
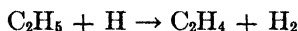
and that the primary split

$$C_2H_6 \rightarrow 2CH_3$$
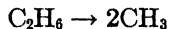
would be expected to be followed largely by recombination to ethane. It seems to the writer that, by analogy with the photosensitized decomposition, the possibility of

$$2C_2H_5 \rightarrow C_4H_{10}$$
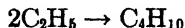
should not be overlooked. In any case this is all speculation at the moment, but the question should soon be settled, since a number of workers are now actively engaged in the photochemistry of the fluorite region.

The mercury-photosensitized decomposition of ethane was first studied by Taylor and Hill (214). They observed that in ethylene–hydrogen

mixtures ethane and higher hydrocarbons were formed. After the pressure change accompanying this reaction was over, other changes occurred which led them to suspect that the ethane formed was being attacked both by hydrogen atoms and by excited mercury. They verified this, and suggested that radicals were undoubtedly involved in the process. Kemula (90) also showed that ethane could be decomposed by excited mercury atoms.

A more thorough investigation of the photosensitized reaction was made by Kemula, Mrazek, and Tolloczko (94), following earlier work by Tolloczko (219). In their investigation the reaction mixture was circulated through a trap at $-80°C.$ to remove the products of higher molecular weight as fast as formed, and thus prevent secondary processes. (This is not a sufficiently low temperature to remove butane efficiently, and hence the prevention of secondary changes was only partially successful.) They found that the decrease in pressure as the reaction went on was accompanied by an exactly parallel increase in the volume of the liquid condensate. The rate was independent of the ethane pressure, but at high pressures a higher percentage of condensate was formed. The gaseous products consisted entirely of hydrogen and methane, the ratio of hydrogen to methane being considerably greater than unity and approaching infinity if the trap were kept at $-20°C.$ instead of $-80°C.$ The condensable products were analyzed by a rough fractional distillation, and were found to consist mainly of butane and octane, with a small amount of hexane and no propane or pentane.

Tolloczko (219) had previously suggested that the mechanism of the process was

$$2C_2H_6 \rightarrow 2C_2H_5 + 2H \rightarrow C_4H_{10} + H_2$$

$$C_2H_6 + C_4H_{10} \rightarrow C_2H_5 + C_4H_9 + 2H$$

$$\rightarrow C_6H_{14} + H_2, \text{ etc.}$$
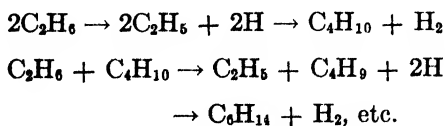
This assumes only a C—H rupture and leads obviously to hydrocarbons with an even number of carbon atoms only. It gives, however, no explanation of the formation of methane. Kemula, Mrazek, and Tolloczko therefore suggest

$$C_2H_6 + Hg^* \rightarrow C_2H_6^* + Hg$$

$$C_2H_6^* \rightarrow C_2H_5 + H$$

$$2C_2H_5 + M \rightarrow C_4H_{10} + M$$

$$2H + M \rightarrow H_2 + M$$

$$C_2H_6 + H \rightarrow C_2H_5 + H_2$$

$$C_2H_6 + H \rightarrow CH_3 + CH_4$$
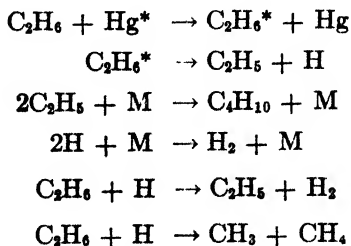
The higher hydrocarbons then result from secondary reactions of butane, etc. The fact that octane is the main higher product obviously suggests that the chief reaction of butane is

$$C_4H_{10} \rightarrow C_4H_9 + H$$

$$2C_4H_9 + M \rightarrow C_8H_{18} + M$$
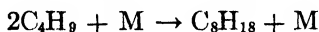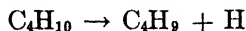
The reaction has recently been reinvestigated by Steacie and Phillips (198). They found that by operating with the trap in the circulation system at a lower temperature it was possible to remove higher products more efficiently, and thus almost completely avoid the occurrence of secondary reactions. The quantum yield and the products obtained at various trapping temperatures as analyzed by low temperature distillation are given in table 1C.

TABLE 1C

The mercury-photosensitized decomposition of ethane (Steacie and Phillips)

TRAPPING TEMPERATURE	QUANTUM YIELD	PRODUCTS IN MOLE PER CENT				
		H_2	CH_4	C_3H_8	C_4H_{10}	Higher hydro-carbons as C_8
°C.						
−70	0 13	47	16	0 0	23	14
−70	0 14	43	23	0.0	20	14
−100	0 11				25	Present
−108	0 095	19 6	44 7	0.0	35 7	Trace
−115	0 098					None
−116	0 090	6 1	59 3	<1 0	34 6	None
−125	0 15	0 0	59.5	21 5	19 0	None
−131	0 18	0.0	58 8	23 5	17 7	None

The most striking thing about these results is that when the conditions are arranged so as to prevent secondary reactions the formation of hydrogen is entirely inhibited. It follows therefore that all the hydrogen formed in previous investigations has resulted from secondary reactions of higher hydrocarbons, and that hydrogen is not a product of the ethane decomposition itself.

Furthermore, previous investigations reported no hydrocarbons with an odd number of carbon atoms (with the exception of methane), and previous mechanisms were formulated mainly for the purpose of explaining this. Table 1C shows, however, that propane is in reality an important product of the reaction. Previous mechanisms are therefore in need of revision.

Steacie and Phillips point out that the two most likely primary processes are:

$$C_2H_6 + Hg(2^3P_1) \rightarrow C_2H_5 + H + Hg(1^1S_0) \tag{1}$$

$$C_2H_6 + Hg(2^3P_1) \rightarrow 2CH_3 + Hg(1^1S_0) \tag{2}$$
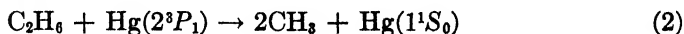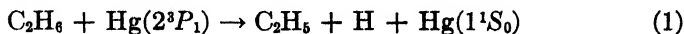
i.e., a C—H or a C—C bond split.

(a) *The C—H bond split.* If the primary reaction is reaction 1, the most likely fate of the hydrogen atoms produced would obviously be to react with ethane,

$$H + C_2H_6 \rightarrow CH_4 + CH_3 \tag{3}$$

$$H + C_2H_6 \rightarrow C_2H_5 + H_2 \tag{4}$$

In order that this mechanism shall yield the products found experimentally it is necessary to assume that reaction 4 is slow compared to reaction 3, since the occurrence of reaction 4 to any appreciable extent would yield far too much butane relative to methane, and would also lead to the production of hydrogen contrary to the experimental findings. As pointed out in the next section, estimates of the relative rates of reactions 3 and 4 are conflicting, but it is possible that the necessary conditions may be fulfilled. We may then assume reaction 3 to be followed by

$$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5 \tag{5}$$

$$CH_3 + C_2H_5 \rightarrow C_3H_8 \tag{6}$$

$$CH_3 + H \rightarrow CH_4 \tag{7}$$

$$2C_2H_5 \rightarrow C_4H_{10} \tag{8}$$

yielding the experimentally found products.

The main difficulty encountered by such a mechanism, however, is the necessity of explaining the absence of hydrogen in spite of the possibility of its formation by the reaction

$$2H \rightarrow H_2 \tag{9}$$

In other words, it must be shown that reaction 3 is fast enough to keep the hydrogen-atom concentration so low that reaction 9 does not occur to an appreciable extent. Steacie and Phillips calculate from the known rates of reactions 3 and 9 that this condition cannot be fulfilled, and therefore rule out the C—H bond split as a possible primary process.

(b) *The C—C bond split.* It appears from the above that the primary process must be a C—C bond split. Steacie and Phillips therefore assume a mechanism in which reaction 2 is followed by reactions 5, 6, and 8,

yielding methane, propane, and butane as the products of the reaction. They explain the low quantum yield of the reaction as partly due to the inefficiency of reaction 2, and partly to the occurrence of the reaction

$$2CH_3 \rightarrow C_2H_6 \qquad (10)$$

which regenerates ethane. (Davis, Jahn, and Burton (29a) conclude from an investigation of the photolysis of azomethane that reaction 10 is slow at ordinary temperatures, but the evidence for this statement is not very conclusive.)

3. The reaction of ethane with hydrogen atoms

Bonhoeffer and Harteck (23) and von Wartenberg and Schultze (231) found that luminescence occurs on mixing hydrogen atoms and ethane, bands due to CH and CC being observed. The major part of the ethane was recovered unchanged, however. The latter authors found that there was a considerable loss of gas in their experiments (up to 25 per cent), which might have been due to methane formed in the reaction, and which with their technique would have passed through the liquid-air trap and been lost. They suggested that the main process was

$$C_2H_6 + H \rightarrow C_2H_5 + H_2$$

$$C_2H_5 + H + M \rightarrow C_2H_6 + M$$
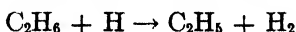
Since a complex mixture of products is not formed, it is apparent that the emission of the CC and CH bands is due to the presence of only minute amounts of C_2 and CH produced by secondary reactions. If the main process went by dehydrogenation to C_2 and CH, it is unthinkable that these could be quantitatively hydrogenated back to ethane without the formation of appreciable amounts of other products.

Chadwell and Titani (29), in the course of another investigation, also made two experiments with ethane and hydrogen atoms. They found that (1) 25 cc. of ethane gave 5 per cent methane, 1.4 per cent carbon dioxide, 1.6 per cent ethylene, and (2) 150 cc. of ethane gave 3 per cent methane, 3 per cent carbon dioxide, and 1.7 per cent ethylene. The carbon dioxide obviously comes from a reaction involving the water or phosphoric acid used to poison the walls of the apparatus. They suggest that the gas lost in the investigation of von Wartenberg and Schultze was ethane, which passed the liquid-air trap, rather than methane. It is certainly to be expected that some ethane would be lost under the experimental conditions of von Wartenberg and Schultze. On the other hand, Kemula (90) found that some methane *was* produced in the reaction of ethane with hydrogen atoms produced by mercury photosensitization.

Steacie and Phillips (196) investigated the reaction of deuterium atoms

with ethane, using the Wood–Bonhoeffer method.   They found an activation energy of 6.3 kg-cal. for the exchange reaction.   They point out that there are three main possibilities for the mechanism of the reaction:
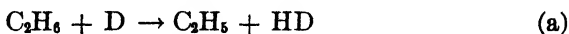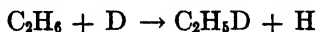
I. Hydrogenation:

$$C_2H_6 + D \rightarrow C_2H_6D \qquad (a)$$

$$C_2H_6D + D \rightarrow C_2H_6 + D_2 \qquad (b)$$

or

$$C_2H_6D + D \rightarrow C_2H_5D + HD$$

II. Dehydrogenation:

$$C_2H_6 + D \rightarrow C_2H_5 + HD \qquad (a)$$

$$C_2H_5 + D \rightarrow C_2H_5D \qquad (b)$$
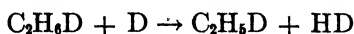
III. Exchange by metathesis:

$$C_2H_6 + D \rightarrow C_2H_5D + H$$

Mechanism III is probably the correct one for the reaction of deuterium atoms with methane as discussed above, and also for the reactions with water, ammonia, etc.   However, since it regenerates one hydrogen atom for each one lost, it cannot account for the "catalytic" destruction of hydrogen atoms by ethane.   Furthermore the activation energy of the ethane–hydrogen atom reaction is so much lower than that of the others that it is apparent that a different mechanism exists.   Mechanism I is very unlikely, since reaction Ia would have to occur at a triple collision (or else have a very low steric factor), and this would make the reaction far too slow to enable ethane to exert a strong catalytic effect on the recombination of hydrogen atoms.   Also, even if reaction Ia occurred sufficiently rapidly, the very unstable molecule C_2H_6D would have little chance of surviving long enough (10^{-6} sec.) to meet a deuterium atom and give Ib.   Hence, in general, reaction Ia would be followed by

$$C_2H_6D \rightarrow C_2H_5 + HD$$

or

$$C_2H_6D \rightarrow C_2H_4D + H_2$$
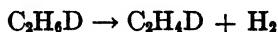
which would make the whole process indistinguishable from reaction IIa, or else by

$$C_2H_6D \rightarrow C_2H_5D + H$$

which would give a result indistinguishable from mechanism III.

Hence they conclude that mechanism II is the correct one, and that the

measured activation energy (6.3 kg-cal.) is that of reaction IIa. They therefore conclude that the companion reaction

$$C_2H_6 + H \rightarrow C_2H_5 + H_2$$
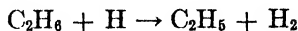
also has an activation energy of the same order of magnitude. This reaction is very important in connection with free-radical mechanisms, and the bearing of its activation energy on the mechanism of the thermal decomposition of ethane will be discussed in the next section.
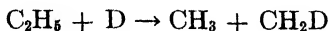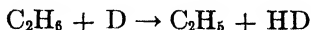
The reaction has recently been reinvestigated by the Wood–Bonhoeffer method by Trenner, Morikawa, and Taylor (226). Their results differ sharply from those of Steacie and Phillips. They conclude that at room temperature the main reaction is

$$C_2H_6 + D \rightarrow CH_3 + CH_3D \qquad (E = 7.2 \text{ kg-cal.})$$

and that the exchange reaction is only appreciable at temperatures from 100°C. up, with an activation energy of 11.4 kg-cal. In their experiments from 10 to 20 per cent of the ethane was found to be decomposed to methane. They made very thorough analyses of the products of the reaction, and determined the deuterium content of each product separately. The methane formed was found to be about 50 per cent deuterized, but the ethane was entirely light at temperatures below 100°C. They suggest that the methane is formed by

$$C_2H_6 + D \rightarrow CH_3 + CH_3D$$

$$CH_3 + D \rightarrow CH_3D^* \rightarrow CH_2D + H$$

They rule out

$$C_2H_6 + D \rightarrow C_2H_5 + HD$$

$$C_2H_5 + D \rightarrow CH_3 + CH_2D$$
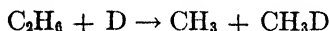
as the mechanism of methane formation, since Taylor and Hill (214) found that in the photosensitized hydrogenation of ethylene

$$C_2H_4 \rightarrow C_2H_5 \rightarrow C_2H_6$$

without the formation of methane. (On the other hand, Klemenc and Patat (96) always obtained methane in the mercury-photosensitized hydrogenation of ethylene.)

Trenner, Morikawa, and Taylor suggest that above 100°C. the reaction also occurs by

$$C_2H_6 + D \rightarrow C_2H_5 + HD$$
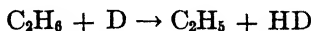
as suggested by Steacie and Phillips. There is, however, a large discrepancy in the activation energy of this process between the two investi-

gations (6.3 and 11.4 kg-cal.). In Steacie and Phillips' investigation the separate products were not isolated, it being assumed from the work of Chadwell and Titani that the formation of methane was negligible. This, however, is not a sufficient explanation of the discrepancy, since to bring the results of the two investigations into line it would be necessary to assume that about 60 per cent of the total ethane present was split into methane at room temperature in Steacie and Phillips' work. In recent work, under conditions similar to those employed by Steacie and Phillips, Steacie (192a) has confirmed the production of methane. At room temperature, however, only about 10 per cent decomposition of ethane occurred, and it appears that further investigation is necessary to determine the cause of the disagreement.

The reaction of ethane with hydrogen atoms has also been investigated qualitatively by photosensitization with mercury (90, 213, 214). It has recently been reinvestigated by Steacie and Phillips (198) by the method described in section IIB(2). It is found that methane, propane, and butane are formed, but no higher hydrocarbons. Hydrogen is consumed. Thus in a typical experiment at a trapping temperature of $-125°C.$, the following stoichiometric equation expresses the results:

$$1C_2H_6 + 0.5H_2 \rightarrow 1.34CH_4 + 0.17C_4H_{10}$$
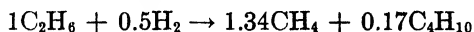
(+ traces of C_3H_8). Steacie and Phillips suggest that the mechanism is

$$Hg(2^3P_1) + H_2 \rightarrow Hg(1^1S_0) + 2H$$

$$H + C_2H_6 \rightarrow CH_4 + CH_3$$

$$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5$$
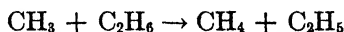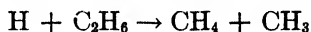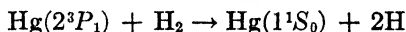
followed by various radical recombination reactions. The possibility of the occurrence of the reaction

$$H + C_2H_6 \rightarrow C_2H_5 + H_2$$
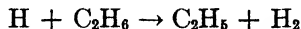
is not ruled out, since the quantum yield of the reaction is low, and if this were followed by

$$C_2H_5 + H \rightarrow C_2H_6$$

the net stoichiometric result would be zero.

4. Free radicals and the ethane decomposition

As we have seen, Rice (156, 166) has suggested that virtually all organic compounds decompose by mechanisms which involve the intermediate formation of free radicals. From a free-radical point of view, the primary step in the ethane decomposition is still a matter of controversy.

Rice and Dooley (160) found that lead mirrors were removed by decomposing ethane at 850° to 950°C. By using standard mirrors, they measured the activation energy of the split into radicals and found a value of 79.5 kg-cal. for the assumed reaction

$$C_2H_6 \rightarrow 2CH_3$$
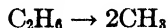
Belchetz and Rideal (8), on the other hand, found no evidence of radical formation, and concluded that the primary reaction was
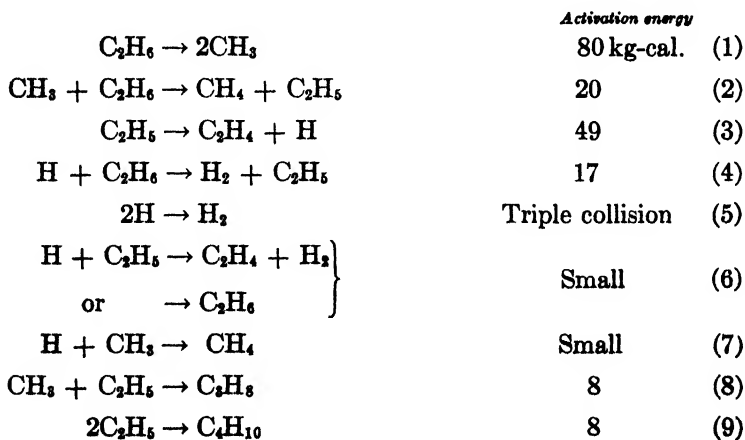
$$C_2H_6 \rightarrow C_2H_4 + H_2$$

with an activation energy of 94.6 kg-cal. They suggest that it is possible that the reaction proceeds through the intermediate formation of ethylidene radicals

$$C_2H_6 \rightarrow CH_3CH + H_2$$

but if so they isomerize to ethylene so rapidly that they cannot be detected. There seems to be no doubt from Rice and Dooley's work that radicals of some sort are formed. It is, of course, possible that they arise in secondary reactions, but the evidence seems on the whole to favor the assumption that at high temperatures the main process is a split into methyl radicals.

Granting that the primary step at high temperatures is a split into methyl radicals, is not, however, a proof that the ordinary thermal decomposition of ethane at low temperatures involves free radicals. Also, as we have seen, if it is to be postulated that the decomposition proceeds by a free-radical mechanism, it is necessary to devise a mechanism which will lead to a first-order rate equation and to an activation energy in agreement with experiment. Rice and Herzfeld (162) suggested that the following mechanism would fulfil these conditions:

		Activation energy	
$C_2H_6 \rightarrow 2CH_3$		80 kg-cal.	(1)
$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5$		20	(2)
$C_2H_5 \rightarrow C_2H_4 + H$		49	(3)
$H + C_2H_6 \rightarrow H_2 + C_2H_5$		17	(4)
$2H \rightarrow H_2$		Triple collision	(5)
$H + C_2H_5 \rightarrow C_2H_4 + H_2$		Small	(6)
or $\rightarrow C_2H_6$			
$H + CH_3 \rightarrow CH_4$		Small	(7)
$CH_3 + C_2H_5 \rightarrow C_3H_8$		8	(8)
$2C_2H_5 \rightarrow C_4H_{10}$		8	(9)

By virtue of reactions 3 and 4 reaction chains will occur, a large number of ethane molecules being decomposed for each primary act. The activation energies allotted to the various steps are partially based on experimental data, qualitative or quantitative, and partially frankly assigned to agree with free-radical mechanisms. Assuming reactions 5, 7, 8, and 9 to be negligible, we get from this scheme

$$E_{\text{overall}} = \tfrac{1}{2} (E_1 + E_3 + E_4 - E_6) = 73 \text{ kg-cal.}$$

in agreement with the measurements of Marek and McCluer. E_1 is the experimental value found by Rice and Dooley for the free-radical split, and E_6 is probably very small, so that these two are fixed. $E_3 + E_4$, however, is merely adjusted to make the mechanism agree with experiment.

For the overall rate of reaction the Rice–Herzfeld scheme leads to the expressions

$$-\frac{\mathrm{d}}{\mathrm{d}t} [C_2H_6] = k[C_2H_6]$$

$$\log k = \tfrac{1}{2} \log \frac{k_1 k_3 k_4}{2k_6}$$

i.e., the reaction is of the first order, as found experimentally. Rice and Herzfeld evaluate the velocity constants of the separate steps by adopting the reasonable approximation that all first-order reactions have rate constants given roughly by $10^{14} e^{-E/RT}$ sec.$^{-1}$, and all bimolecular constants are $10^9 e^{-E/RT}$ liter mol.$^{-1}$ sec.$^{-1}$ On this basis they get for the overall decomposition

$$\log_{10} k = 13.7 - \frac{73{,}000}{2.3RT} \text{ sec.}^{-1}$$

in satisfactory agreement with the experimental equation of Marek and McCluer

$$\log_{10} k = 15.1 - \frac{73{,}200}{2.3RT} \text{ sec.}^{-1}$$

The chain length calculated from the above mechanism is about 100.

It follows therefore that it is *possible* to explain the ethane decomposition on a free-radical basis under all conditions, and it is *known* that a free-radical mechanism largely prevails at very high temperatures.

Recently the work of Patat and Sachsse (137, 175) has thrown considerable doubt upon the idea that the reaction proceeds by a radical chain mechanism. They measured the rate of the ortho–para hydrogen con-

version in the presence of decomposing ethane, and were thus able to detect hydrogen atoms[2] produced by the decomposition or by the reaction

$$CH_3 + H_2 \rightarrow CH_4 + H \qquad (A)$$

The hydrogen atoms produced in this way are being destroyed by reaction 4 above. Hence the stationary concentration of hydrogen atoms is defined by the two processes, and we get approximately

$$\frac{[CH_3]}{[H]} = \frac{k_4[C_2H_6]}{k_A[H_2]}$$

Having evaluated the hydrogen-atom concentration, we can compare it with that calculated from the Rice–Herzfeld mechanism. At 590°C. the experimentally found value is 10^{-11} moles per liter. The value predicted by the Rice–Herzfeld mechanism is about 1000 times larger, viz., 10^{-8} [2]. As pointed out above, Steacie and Phillips determined the activation energy of reaction 4 in the above scheme. They find $E_4 = 6.3$ kg-cal. instead of the assumed value of 17 kg-cal. If we recalculate the hydrogen-atom concentration predicted by the free-radical chain theory, using this value of E_4, we obtain a result which agrees almost exactly with experiment. Such a change in reaction 4, however, seems to introduce insurmountable difficulties into the application of the scheme of Rice and Herzfeld to the ethane decomposition. The overall order of the reaction and the theoretical value of the activation energy are largely dependent on the manner in which the chains are terminated. The change in E_4, by altering the relative concentrations of the reacting substances, upsets the relationships between the rate constants, and it is no longer permissible to neglect reactions 8 and 9. Under these circumstances the scheme no longer predicts a first-order rate or the correct value of the overall activation energy. There has been a certain amount of disagreement between Sachsse (176) and Steacie and Phillips (197) as to the exact manner in which the Rice–Herzfeld mechanism is affected by the results of the latter authors. They are, however, in complete agreement that the main effect of the results is to make the free-radical chain mechanism for the ethane decomposition untenable, at least in its present form.

Of course, as we have seen, the recent work of Trenner, Morikawa, and Taylor (226) disagrees with that of Steacie and Phillips concerning the activation energy of reaction 4. However, even their value of 11.4 kg-cal.

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[2] For a detailed discussion of the ortho–para hydrogen conversion and its use as a method of measuring the stationary concentration of hydrogen atoms in a system, see Farkas (49).
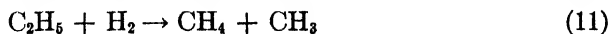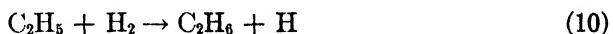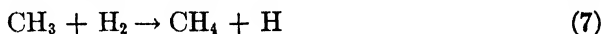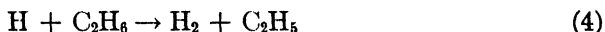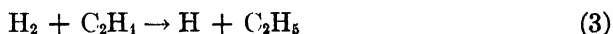
would introduce serious difficulties into the application of the free-radical chain mechanism. Also, on the basis of their work the reaction

$$H + C_2H_6 \rightarrow CH_3 + CH_4$$
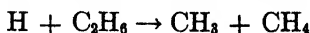
could not be ignored. The presence of this reaction with an activation energy of 7.4 kg-cal. would fundamentally alter the nature of the chain-carrying steps in the Rice–Herzfeld scheme and would destroy its agreement with experiment.

Frost (60) concludes that the scheme is not in agreement with experimental results, and has suggested a new free-radical chain mechanism based on a retarding effect of the unsaturated products of the reaction.

Storch and Kassel (203a) in discussing the free-radical mechanism generalize the Rice–Herzfeld scheme to take into account their new results on the production of methane and propylene. They consider the following scheme:

$$C_2H_6 \rightarrow 2CH_3 \tag{1}$$

$$C_2H_6 \rightarrow C_2H_5 + H \tag{2}$$

$$H_2 + C_2H_4 \rightarrow H + C_2H_5 \tag{3}$$

$$H + C_2H_6 \rightarrow H_2 + C_2H_5 \tag{4}$$

$$H + C_2H_4 \rightarrow C_2H_5 \tag{5}$$

$$H + C_2H_6 \rightarrow CH_4 + CH_3 \tag{6}$$

$$CH_3 + H_2 \rightarrow CH_4 + H \tag{7}$$

$$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5 \tag{8}$$

$$C_2H_5 \rightarrow C_2H_4 + H \tag{9}$$

$$C_2H_5 + H_2 \rightarrow C_2H_6 + H \tag{10}$$

$$C_2H_5 + H_2 \rightarrow CH_4 + CH_3 \tag{11}$$

$$H + C_2H_5 \rightarrow C_2H_6 \tag{12}$$

$$H + C_2H_5 \rightarrow C_2H_4 + H_2 \tag{13}$$

$$C_2H_5 + C_2H_4 \rightarrow CH_3 + C_3H_6 \tag{14}$$

$$2C_2H_5 \rightarrow C_4H_{10} \tag{15}$$

By the customary steady-state method, assuming long chains, they conclude that for the free-radical scheme to agree with experiment the following conditions must be fulfilled:
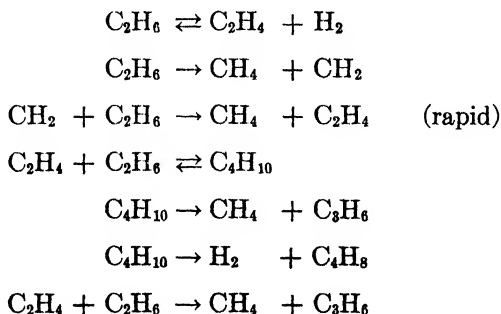
(1) $k_9 \ll k_{10}[H_2]$ for $[H_2] \geq 300$ mm.

(2) $k_9 \gg k_{10}[H_2]$ for $[H_2] \leq 50$ mm.

(3) $k_4[C_2H_6] \gg k_5[C_2H_4]$ for $[C_2H_6] \sim 10[C_2H_4]$

(4) $(k_1 + k_2)[C_2H_6] \gg k_3[H_2][C_2H_4]$ for $\dfrac{[H_2][C_2H_4]}{[C_2H_6]} \leq K_{equil.}$

The first two conditions are incompatible unless the reactions $H_2 +$ C_2H_4 and $C_2H_6 + C_2H_4$ deviate widely from second-order laws, and such a deviation is in definite disagreement with the results of Pease, Sachsse, and Storch and Kassel. Condition 3 is in poor agreement with Rice and Herzfeld's assignment of activation energies, $E_4 = 17$ kg-cal., $E_5 = 10$ kg-cal. The use of $E_4 = 6$ kg-cal., as found by Steacie and Phillips, introduces new difficulties, as discussed above. Storch and Kassel illustrate these difficulties by showing that with $E_4 = 6$ kg-cal., in order that the free-radical mechanism can hold it is necessary that

$$\frac{k_{15}}{k_{12} + k_{13}} < 2 \times 10^{-6}$$

It is extremely unlikely that the rates of two recombination reactions should differ so widely. At present there are no suitable data for testing condition 4.

Storch and Kassel therefore conclude that the free-radical mechanism is ruled out, and that the major part of the observed reaction is to be accounted for by the more or less classical mechanism

$$C_2H_6 \rightleftarrows C_2H_4 + H_2$$
$$C_2H_6 \rightarrow CH_4 + CH_2$$
$$CH_2 + C_2H_6 \rightarrow CH_4 + C_2H_4 \quad \text{(rapid)}$$
$$C_2H_4 + C_2H_6 \rightleftarrows C_4H_{10}$$
$$C_4H_{10} \rightarrow CH_4 + C_3H_6$$
$$C_4H_{10} \rightarrow H_2 + C_4H_8$$
$$C_2H_4 + C_2H_6 \rightarrow CH_4 + C_3H_6$$

In addition, a small amount of reaction undoubtedly occurs by radical and chain processes.

Sickman and O. K. Rice (185) have found evidence that methyl radicals from decomposing azomethane will decompose ethane to some extent. On the other hand, Echols and Pease (38) found that radicals from the ethylene oxide decomposition would not cause the decomposition of

ethane at 425°C., although they would decompose propane and butane. In any case, however, it should be emphasized that the fact that radicals can cause the sensitized decomposition of a substance is no proof that the ordinary decomposition of the substance involves them.

Recently Staveley (188a) has investigated the occurrence of free radicals in the ethane decomposition by the inhibitory effect of nitric oxide. By this method he finds a mean chain length of 12.2 at 620°C. and an ethane pressure of 150 mm. The reaction was followed by the pressure change, but it was proved that possible complications due to the polymerization of ethylene by nitric oxide were absent. The rate of the fully inhibited reaction was found to fall off with diminishing ethane pressure in the ordinary way. Its rate could be expressed by

$$\log_{10} k = 14.44 - \frac{74,500}{2.3RT} \text{ sec.}^{-1}$$

Staveley suggests that comparatively few decomposing molecules give rise to chains, but that these chains are very long, of the order of 10^5 to 10^7 units. In view of the fact that sensitized decomposition of ethane by radicals does not seem to occur easily, such a chain length appears to be very unlikely.

C. Propane

1. The thermal decomposition

The early papers on the propane decomposition by Pease (140), Frey and Smith (59), and others (37, 147, 182) served to establish the fact that the reaction is principally homogeneous and of the first order. The main courses of the reaction are:

$$C_3H_8 \rightarrow C_3H_6 + H_2$$

$$C_3H_8 \rightarrow C_2H_4 + CH_4$$

a certain amount of ethane and butane being also formed.

The first reasonably accurate kinetic data were obtained by Marek and McCluer (118), using a flow method. The products found were those indicated by the above equations in approximately equal amounts. In calculating velocity constants they corrected for the back reactions, and obtained the result

$$\log_{10} k = 13.44 - \frac{62,100}{2.3RT} \text{ sec.}^{-1}$$

The main source of uncertainty in their work was the rather variable temperature of the reaction vessel. Also, as in all work with flow systems,

the effect of pressure on the rate could not be very thoroughly investigated.

Later work by Paul and Marek (139) was done by the same method, but in greater detail. They used small percentage conversions and thus cut secondary reactions down to a minimum. Nitrogen and increased surface were shown to be without effect on the rate when the reaction was carried out in either silica or copper vessels. In the range from 550° to 610°C. the rate is given by

$$\log_{10} k = 16.60 - \frac{74,850}{2.3RT} \text{ sec.}^{-1}$$

Their absolute rates are in rough agreement with those of Marek and McCluer, but, as may be seen from the equations, there is an enormous difference in the temperature coefficient.

Frey and Hepp (58) obtained rates in good agreement with those of Marek and his collaborators. They made very thorough analyses of the products by low-temperature fractional distillation. At 575°C. with a pressure of 739 mm. and a contact time of 74 sec., the products were as follows:

PRODUCTS	MOLE PER CENT	PRODUCTS	MOLE PER CENT
N$_2$	0 50	C$_2$H$_6$	0 49
H$_2$ ..	4.10	C$_3$H$_6$	4.50
CO .		C$_3$H$_8$.	81 75
CO$_2$ . ..		Butadiene . .	
CH$_4$	4.63	Higher hydrocarbons	
C$_2$H$_4$	4.03		

The reaction has also been investigated by Dinzes and Frost (30, 31, 32) by the static method. They followed the reaction by the pressure change from 619° to 666°C. and 1 to 78 mm. It was found that the unimolecular constants drifted badly during an experiment, as discussed above for ethane, the rate in a given run being given by

$$k = \frac{1}{t}\left(\ln \frac{1}{1-x} - 0.921\, x\right)$$

The addition of hydrogen, methane, or ethylene had no effect on the reaction velocity. The freshly formed products of the reaction were found to retard the decomposition of further propane, but if the products were stored for a time they lost their retarding effect. This obviously suggests that the effect is a surface phenomenon of some kind. They interpret all these complications as evidence for a chain process.

The decomposition of propane–propylene–hydrogen mixtures has been investigated by Travers (222c). The results are complex and are not in agreement with those of other workers.

2. Free radicals and the propane decomposition

Rice, Johnston, and Evering (164) showed that free radicals could be detected in the decomposition of propane, and Rice and Johnston (163) found the activation energy of the free-radical split to be 71.5 kg-cal. Rice (157, 159) suggests as a mechanism for the decomposition

$$CH_3CH_2CH_3 \rightarrow CH_3 + C_2H_5$$

$$R + C_3H_8 \rightarrow RH + CH_3CH_2CH_2 \rightarrow RH + C_2H_4 + CH_3$$

$$R + C_3H_8 \rightarrow RH + CH_3CHCH_3 \rightarrow RH + CH_3CH=CH_2 + H$$
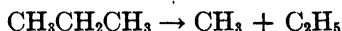
where R represents a hydrogen atom or any radical. From this scheme, making suitable assumptions regarding the relative reactivity of primary and secondary hydrogen atoms, he gets for the overall decomposition

$$6C_3H_8 \rightarrow 6C_2H_4 + 6CH_4$$

$$4C_3H_8 \rightarrow 4C_3H_6 + 4H_2$$

which is in satisfactory agreement with the experimentally found products of the reaction.

Belchetz and Rideal (9) investigated the decomposition of propane on a carbon filament at low pressures, using the technique described above for methane. They concluded that the primary process was

$$CH_3CH_2CH_3 \rightarrow CH_3CH=CH_2 + H_2$$

followed by

$$CH_3CH=CH_2 \rightarrow C_2H_4 + CH_2$$

$$CH_2 + etc. \rightarrow CH_3 + etc.$$
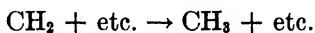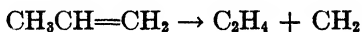
The activation energy of the primary process was found to be 94.2 kg-cal. There is thus a very great discrepancy between their work and that of Rice and his collaborators. Belchetz and Rideal suggest that the methyl radicals found by the latter are secondary products of the methylene radical. On the whole the evidence seems to favor the Rice mechanism for the free-radical split, although the question cannot be considered to be settled. Possibly the carbon filament is the disturbing factor in the experiments of Belchetz and Rideal, as they themselves point out.

The free-radical chain mechanism for the propane decomposition has been tested by Patat (136) by using the ortho–para hydrogen conversion as a test for hydrogen atoms, as described above for ethane. The result is

similar, viz., far too few hydrogen atoms are found as compared with the predictions of the Rice–Herzfeld mechanism. Patat concludes that the maximum possible fraction of the propane molecules which can decompose by a free-radical mechanism as opposed to a direct split into molecules is $10^{-3.2}$ if we assume that the radicals recombine (and thus end the chains) in the gas phase, and is $10^{-1.6}$ if we assume radical recombination on the walls of the reaction vessel. It must therefore be concluded that at low temperatures the Rice mechanism is not in accord with the facts, in spite of its success in predicting the products of the reaction.

There is, on the other hand, ample evidence that radicals can produce a sensitized decomposition of propane. Echols and Pease (38) showed that propane could be decomposed by radicals from the ethylene oxide decomposition at 425°C. They estimated the chain length of the sensitized decomposition by comparing the amount of olefin formed with the carbon monoxide resulting from the ethylene oxide decomposition. The result was $C_nH_{2n}/CO = 0.55$. Of course, this is an average chain length, and it is possible that there are comparatively few long chains rather than a great many short ones.

Sickman and O. K. Rice (185) also found that methyl radicals caused some decomposition of propane, the radicals in this case being produced by decomposing azomethane.

3. Atomic and photochemical reactions

Comparatively little work has been done on atomic or photochemical reactions of propane. By mercury photosensitization Taylor and Hill (213, 214) found that propane reacts faster with hydrogen atoms than does ethane, but more slowly than butane. Recently, in the course of another investigation, Trenner, Morikawa, and Taylor (226) made two runs with propane and deuterium atoms produced by the Wood–Bonhoeffer method. They found that the products of the reaction were mainly methane, together with a small amount of ethane. The amount of decomposition was quite small, being 2.4 per cent at room temperature and about 10 per cent at 109°C. The methane and ethane were found to be highly deuterized, while the propane was not exchanged. Propane is thus much less reactive than ethane, and they find no evidence of a catalytic recombination of hydrogen atoms in the presence of propane, as had been reported previously by Bonhoeffer and Harteck (23). These findings are surprising in view of all previous work in this field, and particularly in view of the fact that Frankenburger and Zell (56) found large decomposition of pentane by hydrogen atoms, indicating increased reactivity with increasing molecular weight of the hydrocarbon. Further work is promised from Taylor's laboratory.

D. *The butanes*

1. The thermal decomposition

As with most of the hydrocarbons, the first data of any kinetic importance were obtained by Pease (140). This investigation was merely a preliminary one, but it served to show that the decompositions of the two butanes were homogeneous and probably of the first order. Pease and Durgan (147), using a flow method, made a more thorough investigation. They concluded that the main reactions which occurred were

$$C_4H_{10} \rightarrow C_4H_8 + H_2 \tag{1}$$

$$C_4H_{10} \rightarrow C_3H_6 + CH_4 \tag{2}$$

$$C_4H_{10} \rightarrow C_2H_4 + C_2H_6 \tag{3}$$
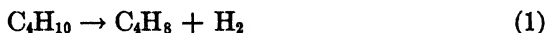
The reactions were found to be not more than 1 per cent heterogeneous, and the rate was slightly increased on diluting the reactants with nitrogen. The unimolecular constants fell off rapidly during the course of an experiment. They suggested that this was perhaps due to a rehydrogenation of the products, since they found that the addition of hydrogen decreased the amount of dehydrogenation. The effect of pressure on the rate indicated that the reactions were predominantly of the first order. The activation energy was found to be roughly 65,000 cal. for both butanes.

Hurd and Spence (79) investigated the reactions by a flow method at 600°C. with the object of ascertaining the products only. They concluded that *n*-butane decomposed by reactions 2 and 3, and isobutane by reactions 1 and 2, and that secondary reactions also occurred to some extent. Cambron (26) concluded that another reaction also occurred in the case of *n*-butane,

$$C_4H_{10} \rightarrow 2C_2H_4 + H_2$$

and that this was, in fact, the predominant reaction at high temperatures. Frey and Hepp (58) investigated the reactions by a flow method at 575°C. They made very thorough analyses of the products by low-temperature distillation, the results of which are given in table 1D.

The reactions were also investigated by Marek and Neuhaus (119, 120), who used various percentage conversions and extrapolated to zero to get the primary process. Their analytical results are given in table 2. In the case of *n*-butane the ratio

$$\frac{C_2H_6 + C_2H_4}{CH_4 + C_3H_6}$$

was in excellent agreement with the predictions of the Rice theory, being 0.71 and 0.79 at 600°C. and 650°C., respectively, as compared with predicted values of 0.75 and 0.79. For isobutane the ratio

$$\frac{CH_4 + C_3H_6}{C_4H_8 + H_2}$$

TABLE 1D

The decomposition of the butanes at 575°C. (Frey and Hepp)

	ISOBUTANE		n-BUTANE	
Pressure, mm	747	77	752	745
Time, sec	39 6		25 2	24 3
Per cent decomposition	17 4	6 7	11 3	10.5
k, sec.$^{-1}$	0 0048		0 0048	0 0046
N_2, mole per cent	0 35	0 95	0 0	0 2
H_2	6 98	3 65	0 84	0 87
CO	0 13	0 09	0 0	0 0
CO_2	0 43		0 0	0 0
CH_4	6 26	2 55	6 38	5 58
C_2H_4	0 33	0 0	3 14	2 84
C_2H_6	0 35	0 13	2 25	2 30
C_3H_6	4 64	1 94	5 85	5.41
C_3H_8	1 47	0 24	0 29	0.39
Butadiene				0.14
$(CH_3)_2C=CH_2$	8 61	3 85		
C_4H_{10}	70 45	86 60	79 95	82 41

TABLE 2

The initial products of the butane decompositions (Marek and Neuhaus)

PRODUCT, IN MOLES PER 100 MOLES REACTING	n-BUTANE		ISOBUTANE	
	At 600°C	At 650°C	At 600°C	At 650°C
CH_4	48 5	48.0	35 0	36 0
C_3H_6	48 5	48 0	34 0	36 0
C_2H_6	34 5	36 7	2 5	1.5
C_2H_4	34 5	38 7		
H_2	16.0	12 3	63 0	63 0
C_4H_8	16 0	12 3	63 0	63 0
C_3H_8	0 0	1 0(?)		

was not in such good agreement. The values found were 0.55 and 0.57, as compared with predicted values of 0.91 and 1.04.

Paul and Marek (139) repeated the investigation from the point of view of the kinetics of the processes. In the temperature range 550° to 610°C. the rates are expressed as follows:

For n-butane: $\log_{10} k = 17.05 - \dfrac{73,900}{2.3RT}$ sec.$^{-1}$

For isobutane: $\log_{10} k = 14.89 - \dfrac{66,040}{2.3RT}$ sec.$^{-1}$

The large difference between the two isomers is noteworthy, if real, but is probably fictitious.

A thorough investigation of the decomposition of n-butane has recently been made by Steacie and Puddington (198a). They used the static

TABLE 3

The decomposition of n-butane (Witham)

TEMPERATURE	CONTACT TIME	k
°C	*seconds*	*sec.*$^{-1}$
600	7.3	0.0145
600	21.8	0.0106
600	58 1	0 0074
600	114 0	0.0044
600	161 2	0.0033
600	210 5	0.0021
650	11.0	0.0598
650	27.0	0.0338
650	37.4	0.0263
650	76.5	0.0098
700	3 0	0.2820
700	12 0	0.0725
700	50 3	0.0097

method and followed the reaction both by pressure change and by analysis at various stages. For the high-pressure rates they obtain

$$\log_{10} k = 12.54 - \frac{58,700}{2.3RT} \text{ sec.}^{-1}$$

There is thus good agreement between their value of the activation energy and that of Frey and Hepp. There is, however, a tremendous discrepancy between these results and those of Paul and Marek. Part of this discrepancy at least is due to Paul and Marek's not having extrapolated their rates to infinite pressure. The products of reaction in Steacie and Puddington's work are also in much better agreement with those of Frey and Hepp than with those of Paul and Marek. The products varied very little with temperature or pressure, mean values of the "initial products"

(i.e., extrapolated to zero conversion) being as follows: CH_4, 35.5 per cent; C_3H_6, 35.5 per cent; C_2H_4, 15.0 per cent; C_2H_6, 14.0 per cent; $H_2 < 1.0$ per cent.

Witham (235) has also measured the rate of decomposition of *n*-butane, alone and mixed with steam. His rates are, in general, lower than those of Marek and his collaborators. His velocity constants for experiments with butane alone are given in table 3. The constants vary so much with contact time that it is impossible to obtain reliable initial rates from his data, or to estimate the magnitude of the activation energy.

2. Free radicals and the butane decompositions

It was shown that free radicals could be detected in the high-temperature decomposition of the butanes by Rice, Johnston, and Evering (164), and the activation energy of the free-radical split was found to be 65.4 kg-cal. for *n*-butane by Rice and Johnston (163). The Rice mechanisms for the reactions are (166) as follows:

For isobutane:

$$C_4H_{10} \rightarrow CH_3 + CH_3CHCH_3$$
$$CH_3CHCH_3 \rightarrow C_3H_6 + H$$
$$C_4H_{10} + R \rightarrow RH + (CH_3)_2CHCH_2$$
$$\rightarrow RH + C_3H_6 + CH_3$$
$$C_4H_{10} + R \rightarrow RH + (CH_3)_3C$$
$$\rightarrow RH + (CH_3)_2C{=}CH_2 + H$$
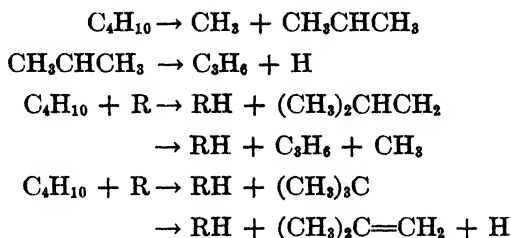
where $R = CH_3$ or H. The usual assumptions as to the relative rates of reactions involving a loss of primary or secondary hydrogen atoms lead to

$$9C_4H_{10} \rightarrow 9CH_4 + 9C_3H_6$$
$$10C_4H_{10} \rightarrow 10C_4H_8 \text{ (iso)} + 10H_2$$
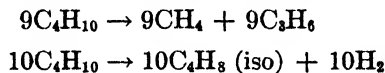
As mentioned above, the agreement with experiment in this case is not very satisfactory.

For n-butane:

$$C_4H_{10} \rightarrow CH_3 + CH_3CH_2CH_2$$
$$C_4H_{10} \rightarrow 2CH_3CH_2$$
$$CH_3CH_2CH_2 \rightarrow C_2H_4 + CH_3$$
$$C_4H_{10} + R \rightarrow RH + CH_3CH_2CH_2CH_2$$
$$\rightarrow RH + C_2H_4 + CH_3CH_2$$
$$C_4H_{10} + R \rightarrow RH + CH_3CH_2CHCH_3$$
$$\rightarrow RH + C_3H_6 + CH_3$$
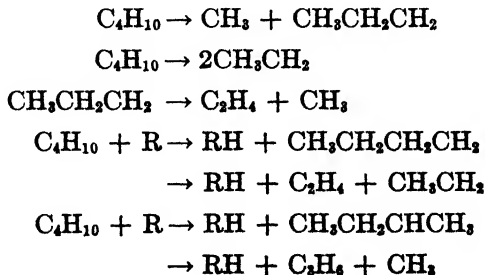
where $R = CH_3$ or CH_3CH_2. This leads to the overall equations

$$6C_4H_{10} \rightarrow 6C_2H_4 + 6C_2H_6$$
$$8C_4H_{10} \rightarrow 8C_3H_6 + 8CH_4$$

in excellent agreement with experiment insofar as the relative amounts of ethylene, propylene, ethane, and methane are concerned. However, the scheme predicts no hydrogen and butene as products, whereas actually Marek and Neuhaus and Frey and Hepp found that from 8 to 16 per cent of the total reaction involved the formation of these substances.

As in the case of ethane and propane, Belchetz and Rideal (9) find a much higher activation energy for the primary split than do Rice and his coworkers, viz., 93.2 kg-cal. They assume for the mechanism

$$C_4H_{10} \rightarrow CH_3CH_2CH{=}CH_2 + H_2$$
$$CH_3CH_2CH{=}CH_2 \rightarrow CH_3CH{=}CH_2 + CH_2$$
$$CH_2 + \text{etc.} \rightarrow CH_3 + \text{etc.}$$
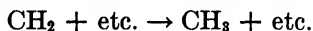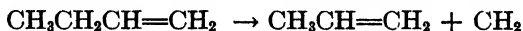
Here again the evidence seems to favor the Rice scheme for the primary split at the high temperatures used.

To what extent the decomposition of the butanes is to be regarded as occurring through free radicals is at the moment an open question. In view of the previous discussion of the ethane decomposition, the free-radical mechanism may well be regarded with suspicion. On the other hand, there is much more evidence in the case of butane to show that chains *can* be set up by radicals. Thus Heckert and Mack (69) found that *n*-butane was "cracked" by decomposing ethylene oxide. Frey (57) showed that 1 per cent of dimethyl mercury at 525°C. could set up chains twenty molecules long in *n*-butane. Echols and Pease (38) found that chains were set up in *n*-butane and isobutane by radicals from the decomposition of ethylene oxide at 425°C. They estimated that the chains were up to twelve molecules long. Sickman and Rice (185) found likewise that *n*-butane was chain decomposed by radicals (presumably methyl) from decomposing azomethane. There thus appears to be no doubt of the possibility of a free-radical chain decomposition of the butanes.

Recently Echols and Pease (39) have reported that the addition of small amounts of nitric oxide inhibits the decomposition of *n*-butane. Thus at 500°C. in a potassium chloride-coated bulb, with an initial pressure of butane of 200 mm., they obtain the following results:

P_0 (NO)	INITIAL RATE OF DECOMPOSITION OF C_4H_{10}	PER CENT DECOMPOSITION IN 120 MINUTES AS INFERRED FROM	
		Pressure change	Analysis
mm.			
0	1.0	26.5	31
20	0.05	7.1	13

They therefore conclude that nitric oxide is functioning as a chain breaker (188a, 189, 190), and hence that the ordinary butane decomposition involves chains. Preliminary observations by Steacie and Folkins (194) are in agreement with these results.

3. Atomic and photochemical reactions

There has been little work on the reaction of hydrogen atoms with the butanes. Taylor and Hill (213, 214) found, using mercury photosensitization, that butane reacts faster with hydrogen atoms than propane, which in turn reacts faster than ethane. Recently Trenner, Morikawa, and Taylor (226) have made one run with n-butane and deuterium atoms produced by the discharge tube method. They find about 11 per cent decomposition at 110°C. to give methane, ethane, and propane. The methane and ethane are highly exchanged, while the recovered butane is not exchanged at all. This is an unexpected result, for the reasons mentioned in the discussion of the propane reaction.

Steacie and Phillips (198) in the course of another investigation made one run on the mercury-photosensitized decomposition of butane. They found that hydrogen and higher hydrocarbons were produced in large amounts. The quantum yield at room temperature was 0.55.

E. The higher paraffins

These reactions are too complicated to be of much value from a kinetic standpoint, and are considered to be, in general, beyond the scope of this review. There are, however, a few investigations which are of interest by comparison with the lower paraffins, and they will be briefly mentioned. No attempt will be made to discuss the products of the decompositions of the higher paraffins.

Pease and Morton (148) investigated the decomposition of n-heptane. The investigation was not very thorough, but it showed that the reaction is homogeneous and of the first order. The rate was unaffected upon changing the surface of the reaction vessel, but complicating secondary processes were undoubtedly present. Their results are expressed by the equation

$$\log_{10} k = 9.85 - \frac{46,500}{2.3RT} \text{ sec.}^{-1}$$

As pointed out later, however, there is no doubt that their value of the activation energy is greatly in error. The same authors also investigated the decompositions of a number of cyclic and aromatic hydrocarbons.

Frey and Hepp (58) investigated the decomposition of a number of higher hydrocarbons by a flow method, but their data are not in general

sufficient to enable a very reliable estimate of the activation energy. They concluded that compounds with tertiary carbon atoms decompose faster than others. They give the following velocity constants at 425°C. for some of the simpler compounds: n-butane, 1.9×10^{-6} sec.$^{-1}$; n-pentane, 2.4×10^{-6} sec.$^{-1}$; isopentane, 3.7×10^{-6} sec.$^{-1}$; n-hexane, 1.1×10^{-5} sec.$^{-1}$

Dinzes and his collaborators (33, 34) have investigated the kinetics of the decomposition of n-hexane and n-octane. They obtained results similar to those already discussed for ethane and propane. The velocity constants are given as follows:

$$\text{For } n\text{-hexane:} \quad \log_{10} k = 14.58 - \frac{64,500}{2.3RT} \text{ sec.}^{-1}$$

$$\text{For } n\text{-octane:} \quad \log_{10} k = 14.70 - \frac{64,900}{2.3RT} \text{ sec.}^{-1}$$

They also investigated (33a) the decomposition of dodecane, 2,2,4-trimethylpentane, and 2,5-dimethylhexane, but all these reactions appear to be too complex to yield much information.

Bairstow and Hinshelwood (3) have investigated the homogeneous catalysis of the decomposition of n-hexane by iodine. The results are somewhat uncertain, and are not easy to interpret.

Rice and Polly (165) obtained cyclohexane from the decomposition of diheptyl mercury. They discuss the formation of alicyclic hydrocarbons from free radicals, and conclude that in this case the process is probably

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2 \rightarrow H_2C \underset{CH_2CH_2}{\overset{CH_2CH_2}{\diagup \diagdown}} CH_2 + CH_3$$
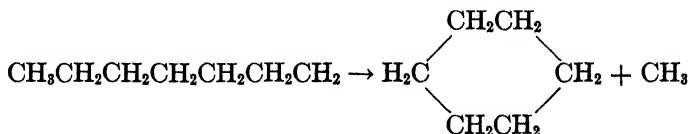
Klemenc and Patat (97) investigated the mercury-photosensitized reactions of n-pentane. They found that decomposition and polymerization both occurred, hydrogen, methane, and other hydrocarbons being formed. Similar results were obtained by Frankenburger and Zell (56), who concluded that the primary process must involve the splitting of both C—H and C—C bonds.

A brief investigation of the mercury-photosensitized decomposition of n-hexane was made by Taylor and Bates (209). Much hydrogen and some methane were formed in the reaction.

F. Comparison of the paraffin decompositions

The kinetic data for the thermal decomposition of the paraffins are summarized in table 4. As is usually the case, the exponential and non-

exponential factors in the rate expression $k = Ae^{-E/RT}$ are interdependent, and their mutual fluctuations mask regularities in the data which might otherwise appear. In order to avoid this, and also to enable comparison

TABLE 4

Summarized kinetic data for the decomposition of the paraffins

SUBSTANCE	$\log_{10} A$	E	k_{425}	k_{575}	OBSERVER
		cal. per mole	sec.$^{-1}$	sec.$^{-1}$	
CH$_4$	12 00	79,385	1.3×10^{-13}	3.3×10^{-9}	Kassel (86)
C$_2$H$_6$	15 12	73,200	1.5×10^{-8}	1.7×10^{-4}	Marek and McCluer (118)
	16 06	77,700	5.1×10^{-9}	1.0×10^{-4}	Recalculated (139)
	14 1	69,800	1.6×10^{-8}	1.2×10^{-4}	Sachsse (174)
				$1.0 \times 10^{-4*}$	Storch and Kassel (203a)
C$_3$H$_8$		(65,000)			Pease and Durgan (147)
				1.5×10^{-3}	Frey and Hepp (58)
	13 44	62,100	9.6×10^{-7}	2.6×10^{-3}	Marek and McCluer (118)
	16 60	74,850	1.4×10^{-7}	1.9×10^{-3}	Paul and Marek (139)
n-C$_4$H$_{10}$		(65,000)			Pease and Durgan (147)
	13.53	61,400	1.9×10^{-6}	4.8×10^{-3}	Frey and Hepp (58)
	17 05	73,900	7.8×10^{-7}	9.8×10^{-3}	Paul and Marek (139)
	12 54	58,700	1.5×10^{-6}	2.6×10^{-3}	Steacie and Puddington (198a)
iso-C$_4$H$_{10}$		(65,000)			Pease and Durgan (147)
				4.8×10^{-3}	Frey and Hepp (58)
	14.89	66,040	1.5×10^{-6}	7.1×10^{-3}	Paul and Marek (139)
n-C$_5$H$_{12}$	13 4	61,200	2.4×10^{-6}	5.7×10^{-3}	Frey and Hepp (58)
iso-C$_5$H$_{12}$	12.93	58,600	3.7×10^{-6}	6.5×10^{-3}	Frey and Hepp (58)
n-C$_6$H$_{14}$	12.43	55,500	1.1×10^{-5}	1.3×10^{-2}	Frey and Hepp (58)
	14.58	64,500	2.3×10^{-6}	8.7×10^{-3}	Dinzes et al. (33, 34)
2,3-Di-methyl-butane				1.9-2.4×10^{-2}	Frey and Hepp (58)
n-C$_7$H$_{16}$	9.85	46,500	1.9×10^{-5}	7.1×10^{-3}	Pease and Morton (148)
n-C$_8$H$_{18}$	14 70	64,900	2.3×10^{-6}	9.1×10^{-3}	Dinzes et al. (33, 34)

* Inferred by comparison with reference 139 at 565°C.

with the results of Frey and Hepp, the velocity constants have been calculated from the equations given by other observers for temperatures of 425°C. and 575°C., and activation energies have been calculated from

Frey and Hepp's results at these two temperatures. The first of these temperatures is below the usual experimental range for these reactions, while the latter is well within it. It will be seen from the table that there is fair agreement throughout at 575°C., but the calculated rates at 425°C. show large discrepancies. Thus in the case of propane, the results of Frey and Hepp and of Paul and Marek are in good agreement, and those of Marek and McCluer agree within a factor of 2 at 575°C. At 425°C., however, the results of the two latter disagree by a factor of 7. The reason, of course, is that the tremendous discrepancy of 13,000 cal. in the activation energy is balanced by a difference of a factor of over 1000 in A, so that the farther one gets from the experimental temperature range the greater is the discrepancy. It must be concluded, therefore, that in the neighborhood of 600°C. the absolute rates of the reactions are well established, but that with the exception of methane and ethane the activation energies are almost all untrustworthy.

Frey and Hepp's work constitutes the longest single set of observations and their individual results should be strictly comparable. Unfortunately, however, almost all their work was done at only two temperatures, and hence the activation energies calculated from their results are not very reliable. Their work, however, seems to indicate that the activation energies of the hydrocarbons from propane to octane are definitely lower than those for methane and ethane, but do not differ much among themselves. By comparison with other work, Paul and Marek's values of E for propane and n-butane appear to be too high, while Pease and Morton's value for n-heptane is definitely far too low. These conclusions receive support from the fact that an A factor of 10^{17} is unusually large and one of 10^9 is unusually small for a unimolecular decomposition, so that errors in the A factors in these cases apparently compensate errors in E.

In a recent review Frey (57) has plotted log (rate)$-1/T$ curves for the decomposition of various hydrocarbons, including mixtures such as "gas oil." The curves plotted correspond roughly to the paraffins from C_1 to C_{17}. It is noteworthy that the slopes of the curves (i.e., the values of E) from C_3 to C_{17} are virtually identical, although of course the points are widely scattered. Existing information, however, is much too inaccurate to permit any definite conclusions to be drawn.

As far as the absolute rates of decomposition are concerned, the very great stability of methane is noteworthy. Ethane is also considerably more stable than propane, but the higher members of the series do not differ greatly. Thus, taking Marek and McCluer's recalculated value for ethane as unity, the relative rates of decomposition at 575°C. are given in table 5.

The activation energies of the split into free radicals as determined by

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Rice and his collaborators are summarized in table 6. The rapid drop in the activation energy with increasing molecular weight is noteworthy. It is evident that for the higher members of the series, say from butane on, the activation energies of the free radical and the ordinary overall thermal decomposition are not very different. It is therefore possible that, in spite of the evidence against the free-radical mechanism for ethane and

TABLE 5

Relative rates of decomposition of the paraffins at 575°C.

SUBSTANCE	k_{575} (AVERAGE OF THE VALUES OF DIFFERENT OBSERVERS)
	sec.$^{-1}$
CH_4	3.3×10^{-5}
C_2H_6	1.0
C_3H_8	17
n-C_4H_{10}	73
iso-C_4H_{10}	60
n-C_5H_{12}	57
iso-C_5H_{12}	65
n-C_6H_{14}	109
n-C_7H_{16}	71
n-C_8H_{18}	91

TABLE 6

Activation energies of the split into free radicals (Rice et al.)

SUBSTANCE	E
	kg-cal.
CH_4	100
C_2H_6	79.5
C_3H_8	71.5
n-C_4H_{10}	65.4
n-C_5H_{12}	64.0
n-C_7H_{16}	63.2

propane, the higher members may actually decompose by some process involving radicals. It is unfortunate that the values of the activation energies of the ordinary thermal decompositions are so unreliable that one cannot compare them with the free-radical activation energies with any degree of certainty.

One reason for uncertainty, of course, is that we are really dealing with several different simultaneous reactions in the case of the higher hydrocarbons. Marek and Neuhaus (120) have summarized the separate velocity constants for these reactions (estimated from the results of Marek

and his coworkers) in the case of ethane, propane, and butane. The data are given in table 7.

It is illuminating to calculate the activation energies of the various splits from these data, and the results of such calculations are given in table 8. It has already been pointed out that there is considerable doubt

TABLE 7

Velocity constants of the separate reactions of the paraffins

(Summarized by Marek and Neuhaus)

SUBSTANCE	TEMPERATURE	k FOR SPLITTING OFF		
		H_2	CH_4	C_2H_6
	°C	sec.$^{-1}$	sec.$^{-1}$	sec.$^{-1}$
C_2H_6	575	0 00019		
	600	0 00066		
	625	0.00205		
	650	0.00650		
	675	0 01850		
C_3H_8	550	0 00026	0 00019	
	575	0 00100	0 00076	
	600	0 00360	0 00274	
	625	0 01175	0.00895	
	650	0 03725	0 02830	
	675	0 11000	0 08360	
n-C_4H_{10}	525	0.000096	0 00029	0 000207
	550	0 00040	0.00121	0 000863
	575	0.00157	0 00475	0 00338
	600	0 00552	0 01671	0 01190
	625	0 01540	0 05330	0 04050
	650	0.04610	0 18000	0 13900
iso-C_4H_{10}	550	0 00132	0 000735	
	575	0 00454	0 00252	
	600	0.01368	0 00759	
	625	0 03750	0 02083	
	650	0.10400	0 05880	

whether the difference in the activation energies for *n*-butane and isobutane is real or not. (Although it should be noticed that the results of Frey and Hepp for *n*-pentane and isopentane show the same trend.) If we leave the isobutane results out of consideration, the striking thing about the remainder is that they are all probably identical within the experimental error. To split off hydrogen requires the breaking of two C—H bonds and the changing of one C—C to C=C. To split methane, on the other

hand, requires the breaking of one C—H and one C—C and the changing
to one C—C to C=C. In view of the difference in the C—H and C—C
bond strengths, a considerable difference in the activation energies might
have been anticipated   There is no doubt that a more accurate determina-
tion of these activation energies for the whole series would be of the
greatest interest

In discussing the variation in rate as we ascend the series, Pease and
Morton (148) point out that $E/\log A$ is approximately constant and equal
to 4500 for all the paraffins. It is, however, very doubtful if this means
more than the fact that E and A in any given case are affected by com-
pensating errors, while the absolute rate of reaction varies very little.

There have been a number of papers which discuss the decomposition
of the paraffins in a general way. Thus Burk (24) has attempted to

TABLE 8

*Activation energies of the separate decomposition reactions of the paraffins calculated
from the data of table 7*

SUBSTANCE	E FOR SPLITTING OFF		
	H_2	CH_4	C_2H_6
	kg-cal	*kg-cal*	*kg-cal.*
C_2H_6	73 2		
C_3H_8	74 2	75 4	
n-C_4H_{10}	70 2	75.4	76 6
iso-C_4H_{10}	65 7	65 7	

derive a general expression for the rate for all the members of the series.
He starts from the Polanyi–Wigner expression for a first-order reaction and
obtains the equation

$$k = (n - 2) \, \nu e^{-E/RT}$$

for the decomposition of a hydrocarbon containing n carbon atoms. ν is
the frequency of the C—C valence vibrations, assumed constant for all the
hydrocarbons, and E is also assumed to be constant. The relative rates
calculated in this way are in rough agreement with experiment.   It should
be remembered, however, that any equation which makes the rate increase
slowly as we ascend the series will give approximate agreement with ex-
periment. It is probable that the main cause of the increased rate is
really to be found in a slowly diminishing bond strength, and hence activa-
tion energy, as we ascend the series. (For a detailed discussion of this
effect in another series of compounds see Steacie and Katz (195).)

Kassel (87) has pointed out in a note that the assumption of 1,4-de-

hydrogenation as the main mechanism of hydrocarbon decomposition, together with lesser amounts of 1,2- and 1,1-dehydrogenation, will account for all the products predicted by the free-radical theory.

There have been a number of recent reviews of the decomposition reactions of the paraffins, among which may be mentioned those of Schmidt (181), Frey (57), Egloff and Wilson (48), and especially the monograph by Egloff (40). In all of these attention is mainly focussed on the products of the reactions, rather than the kinetics of the processes. Thermodynamic and thermochemical data for the paraffins have been summarized by Rossini (172a), and by Thomas, Egloff, and Morrell (218a).

III. THE OLEFINS

On account of the fact that the olefins both decompose and polymerize when heated, their reactions are much more complex than those of the paraffins, and from a kinetic point of view we are on much less certain ground. The literature on the qualitative aspects of the subject is enormous, and we shall touch only on those papers which have some bearing on the main kinetic details of the processes.

A. Ethylene

1. The polymerization and decomposition of ethylene

If ethylene is heated to a moderately low temperature the main reaction is polymerization. At higher temperatures it also undergoes decomposition. It is, in general, not possible to separate completely the two reactions, and hence the whole situation is complex. We shall consider the low-temperature reactions first, since they are the simpler. Insofar as the older work and theories of polymerization are concerned, reference may be made to the review of Egloff, Schaad, and Lowry (46), and to the comprehensive monograph of Egloff (40).

Hague and Wheeler (67, 68), on the basis of experiments complicated by a considerable amount of decomposition, concluded that butadiene was the fundamental intermediate substance in the polymerization of ethylene, the reactions being

$$2C_2H_4 \rightarrow CH_3CH_2CH=CH_2$$

$$\rightarrow CH_2=CH-CH=CH_2 + H_2$$
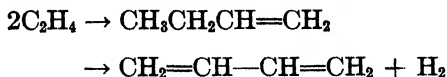
the butadiene then reacting further with ethylene to give benzene, etc. The same conclusion was reached by Wheeler and Wood (233).

Pease (142, 143, 145), in the first investigations of any value for our purpose, found that by working at pressures of about 10 atm. it was possible to suppress the decomposition almost completely, and to obtain

as products practically nothing but higher olefins. At lower pressures the reaction was complex, but at high pressures it was definitely a second-order association reaction, with an activation energy of 35,000 cal. The rate of reaction was low for a process with such an activation energy, and it was necessary to assume a steric factor of about 1/2000. This is, of course, rather to be expected on account of dreierstoss restrictions. Pease suggested for the mechanism

$$2C_2H_4 \rightarrow C_4H_8$$

followed by

$$C_2H_4 + C_4H_8 \rightarrow C_6H_{12}, \text{ etc.}$$
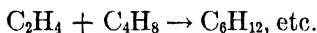
It was found by Storch (201) that the reaction is greatly accelerated by traces of oxygen. The products were analyzed by low-temperature fractional distillation, a typical analysis from a run at 377°C. being given in table 9. Storch obtained an activation energy of 42,000 cal., a value somewhat higher than that of Pease. He suggests that this is due to the

TABLE 9

Products of the ethylene polymerization at 377°C (Storch)

SUBSTANCE	VOLUME PER CENT
Propylene	13 8
Butylene	31 7
Cyclobutane (perhaps a mixture)	12.6
Pentenes	4 1
"Cyclopentane"	8 1
Hexenes	12 6
Higher olefins.	10 1
Unaccounted for (perhaps adsorbed by stopcock grease, etc.)	7 0

presence of traces of oxygen in the ethylene used by Pease. For the mechanism he accepts Pease's suggestion that the primary step is

$$2C_2H_4 \rightarrow C_4H_8$$

He then assumes secondary reactions of the following types:

$$C_2H_4 + C_4H_8 \rightarrow 2C_3H_6, \text{ or}$$
$$C_2H_4 + C_4H_8 \rightarrow C_6H_{12}$$
$$C_2H_4 + C_3H_6 \rightarrow C_5H_{10}$$
$$C_2H_4 + C_5H_{10} \rightarrow C_3H_6 + C_4H_8, \text{ or}$$
$$C_2H_4 + C_5H_{10} \rightarrow C_7H_{14}$$
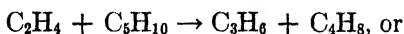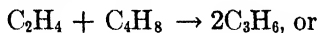
Some change in the mechanism suggested by Pease is, of course, necessary, since it leads only to olefins with an even number of carbon atoms, and Storch found considerable amounts of C_3 to C_5 hydrocarbons. As Storch points out, there are not, as yet, nearly enough data to enable us to sort out all these reactions.

In a later paper (202) Storch reports an attempt to purify ethylene sufficiently to enable really reproducible results to be obtained. This was not successful, but he found that the addition of small amounts of ethyl mercaptan slowed down the average rate and made the results strictly reproducible. Further, it was found that these rates were in good agreement with the slowest rates obtained with "pure" ethylene. This suggests the presence of a catalyst of some sort under normal conditions, and he considers that the reaction is probably not a simple bimolecular change. While it is not yet certain what the initial step is, butylene probably precedes propylene as a product. The activation energy of the overall reaction is found to be 43,500 cal., in good agreement with his former estimate.

At the moment it seems difficult to assess the situation, since the results of Pease were so consistent that it does not seem to be justifiable to assume that they were largely influenced by fortuitous traces of impurities without further proof.

The reaction has also been investigated by Krauze, Nemtzov, and Soskina (98, 100), who find it to be homogeneous and of the second order. Their results can be expressed by the equation

$$\log_{10} k = 10.85 - \frac{37,700}{2.3 RT} \text{ liter mol.}^{-1} \text{ sec.}^{-1}$$

Their value of the activation energy is thus rather closer to the value of Pease than to that of Storch. They find that the second-order velocity constants fall off considerably during an experiment. They calculate a collision efficiency of 1/400, which is somewhat higher than Pease's value.

A few experiments on the polymerization of ethylene have also been made by Travers and Hockin (224).

The reaction at higher temperatures is much more complex, and consists of both decomposition and polymerization. It was shown by Frey and Smith (59) to be homogeneous in silica vessels. A typical analysis of the products of the reaction at 575°C. and 1 atm. pressure, after 4 min. reaction time, is given in table 10. These results correspond to a velocity constant of about 0.0011 sec.$^{-1}$ if the reaction is assumed to be a first-order decomposition. Frey and Smith found that the addition of hydrogen to the reactant decreased the amount of unsaturated products formed, which

suggests that secondary hydrogenation reactions play a part (the hydrogen being normally produced from the decomposition).

Wheeler and Wood (233) obtained the products shown in table 11 at various temperatures and with contact times of from 10 to 20 sec. Their analyses are not in very good agreement with those of Frey and Smith or of Schneider and Frolich (182).

TABLE 10

Products of the ethylene decomposition (and polymerization) at 575°C
(Frey and Smith)

SUBSTANCE	PER CENT	SUBSTANCE	PER CENT
N_2	0 8	C_3H_8	0 0
H_2	0 8	C_4H_8	1 2
CH_4	2 6	C_5 to C_8	2 2
C_2H_4	84 4	Higher hydrocarbons	0 3
C_2H_6	3 2		

TABLE 11

Products of the ethylene decomposition at various temperatures (Wheeler and Wood)

TEMPERATURE	VOLUME PER CENT						
	H_2	CH_4	C_2H_6	C_2H_4	C_3H_6	C_4H_8	C_4H_6
°C.							
650	0 7	0 5	2 0	89 9	0 0	3 8	0.3
700	3 2	4 9	4 9	66.2	2 2	2 8	0 4
750	7 2	16 7	8 6	47 6	1 7	1 5	0 2
800	17.3	33 7	6 9	29 0	1 1	0 0	0 15
850	35 8	49 7	3.3	12 2	0.5		
900	51 0	55 2	2 2	4 6	0 0		

In a recent paper Burk, Baldwin, and Whitacre (25) report an investigation at 625°C. The products of the reaction were similar to those of Frey and Smith The reaction was homogeneous, with an order slightly greater than one. They review the proposed mechanisms in some detail, and suggest that the results can best be interpreted by assuming that polymerization and decomposition both occur, i.e.

$$2C_2H_4 \rightarrow C_4H_8 \qquad (a)$$

$$C_2H_4 \rightarrow C_2H_2 + H_2 \qquad (b)$$
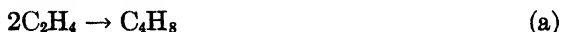
reaction b being followed by further reactions of acetylene to give butadiene, etc.

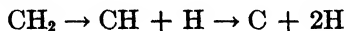Egloff, Schaad, and Lowry (46) suggest that the primary reaction is

$$C_2H_4 \rightarrow 2CH_2$$
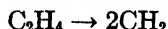
The higher hydrocarbons then result from reactions of the type

$$CH_2 + C_2H_4 \rightarrow C_3H_6$$

$$CH_2 + C_3H_6 \rightarrow C_4H_8$$

and also perhaps from the direct reaction

$$2C_2H_4 \rightarrow C_4H_8$$
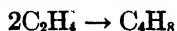
In addition they assume

$$CH_2 \rightarrow CH + H \rightarrow C + 2H$$

acetylene being formed by

$$2CH \rightarrow C_2H_2$$
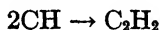
Ethane is assumed to be formed by direct hydrogenation of ethylene.   It should be pointed out, however, that Rice and his collaborators have been consistently unsuccessful in attempts to prepare radicals from decomposing ethylene, and Rice assigns an activation energy of 150 kg-cal. to the reaction
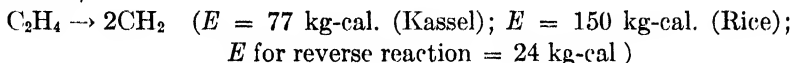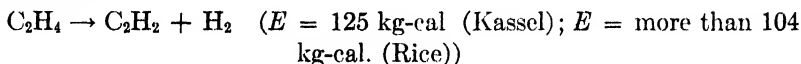
$$C_2H_4 \rightarrow 2CH_2$$

which would rule it out as the primary step.   However, as previously pointed out, the Rice technique is perhaps not very successful in detecting methylene radicals, and this estimate of the activation energy may be altogether too high.   Kassel assigns a value of 77 kg-cal. to the reaction, which would make it a feasible primary process.

Egloff and Wilson (48) have recently reviewed the thermal reactions of the hydrocarbons.   They base practically everything on the reactions of ethylene, which they assume to be the key substance in hydrocarbon chemistry.   They suggest that the following five primary reactions of ethylene are the fundamental ones, all other products being assumed to be due to secondary processes, of which there are a very large number.
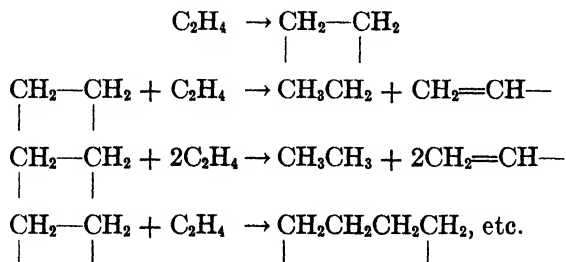
Reaction 1:

$$2C_2H_4 \rightarrow CH_3CH_2CH=CH_2 \quad (E = 35 \text{ kg-cal.})$$
$$+ C_2H_4 \rightarrow \text{cyclic products}$$
$$+ H_2 \quad \rightarrow C_2H_6 + C_2H_4$$
$$+ H_2 \quad \rightarrow C_4H_{10}$$
$$+ H_2 \quad \rightarrow CH_4 + CH_3CH=CH_2$$

Reaction 2:
$$2C_2H_4 \rightarrow 2H + 2CH_2{=}CH \quad (E = 104 \text{ kg-cal.})$$
$$\rightarrow CH_2{=}CH{-}CH{=}CH_2$$
$$+ C_2H_4 \rightarrow \text{higher hydrocarbons and cyclic compounds}$$

Reaction 3:
$$C_2H_4 + H_2 \rightarrow C_2H_6 \quad (E = 43 \text{ kg-cal.}; E \text{ for the reverse reaction } = 73 \text{ kg-cal.})$$
$$\rightarrow 2CH_3 \quad (E = 80 \text{ kg-cal.})$$
$$+ H \rightarrow H_2 + C_2H_5 \quad (E = 17 \text{ kg-cal.})$$
$$\rightarrow H + C_2H_5 \quad (E = 98 \text{ kg-cal})$$

Reaction 4:
$$C_2H_4 \rightarrow 2CH_2 \quad (E = 77 \text{ kg-cal. (Kassel)}; E = 150 \text{ kg-cal. (Rice)};$$
$$E \text{ for reverse reaction } = 24 \text{ kg-cal})$$

Reaction 5:
$$C_2H_4 \rightarrow C_2H_2 + H_2 \quad (E = 125 \text{ kg-cal (Kassel)}; E = \text{more than } 104 \text{ kg-cal. (Rice)})$$
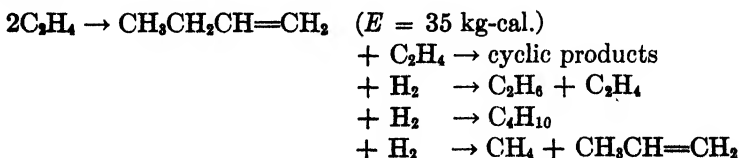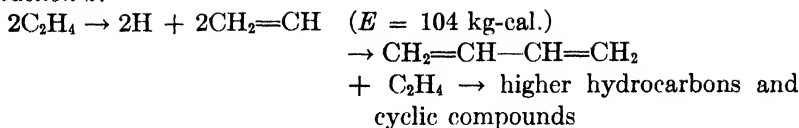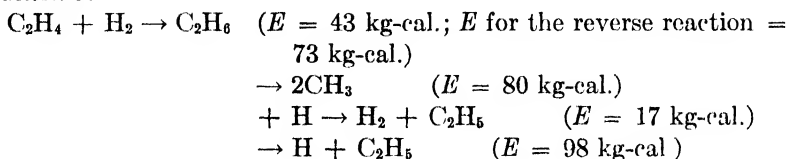
In view of the previous discussion of some of these reactions in this review, it will be apparent that a number of these activation energies are open to question. Furthermore, the whole scheme is very speculative, and it remains to be seen whether or not free radicals really play the important rôle assumed by Egloff and Wilson. Their scheme is interesting, however, whether true or not, in that it emphasizes the tremendous variety of possible secondary reactions.

Hurd (78), in a review of the pyrolysis of unsaturated hydrocarbons, favors the "bond opening" type of mechanism, viz.,

$$C_2H_4 \rightarrow CH_2{-}CH_2$$
$$\overset{|}{} \quad \overset{|}{}$$

$$CH_2{-}CH_2 + C_2H_4 \rightarrow CH_3CH_2 + CH_2{=}CH{-}$$
$$\overset{|}{} \quad \overset{|}{}$$

$$CH_2{-}CH_2 + 2C_2H_4 \rightarrow CH_3CH_3 + 2CH_2{=}CH{-}$$
$$\overset{|}{} \quad \overset{|}{}$$

$$CH_2{-}CH_2 + C_2H_4 \rightarrow CH_2CH_2CH_2CH_2, \text{ etc.}$$
$$\overset{|}{} \quad \overset{|}{} \qquad \overset{|}{} \qquad \overset{|}{}$$

It seems to the writer to be open to question whether mechanisms of this sort have any real physical significance, although they have been frequently suggested for various reactions (14, 15).

It will be apparent from the foregoing discussion that our knowledge of the thermal reactions of ethylene in the temperature range from 500° to 900°C. is very fragmentary, and little is known with certainty.

At still higher temperatures the reaction again becomes simpler, according to an investigation of Fischer and Pichler (54). At temperatures in the neighborhood of 1400°C. and at low pressures the reaction is almost completely a straight dehydrogenation to acetylene. The data of Fischer and Pichler have been recalculated by Storch (200).

2. The thermal hydrogenation of ethylene

The equilibrium

$$H_2 + C_2H_4 \rightleftarrows C_2H_6$$

was investigated by Pease and Durgan (146). The formation of methane in a side reaction was a serious complication and affected the accuracy of the results. They found that the equilibrium constant (pressures in atmospheres) given by

$$K_{atm.} = \frac{[C_2H_4][H_2]}{[C_2H_6]} \cdot \frac{P}{100}$$

had the values

T in °C.	$K_{atm.}$
600	0.0310
650	0.082
700	0.20

or,

$$\Delta F = -RT \ln K = 31{,}244 - 28.88\ T$$

Frey and Huppke (58b) have also investigated the equilibrium, its attainment being catalyzed by passing the gases over chromium oxide. They obtained the following values of the equilibrium constant

T in °C.	$K_{atm.}$
400	0.00015
450	0.00076
500	0.0032

Their results can be expressed by

$$\Delta F = 27{,}798 - 9.21\ T \log_{10}T + 2.17\ T$$

Their values have been recalculated by Kistiakowsky, Romeyn, Ruhoff, Smith, and Vaughan (95a), who give more weight to experiments at short

contact times and thus cut down the effects of secondary changes. They thus obtain

$K_{atm.}$	T in °C.[3]
8.2×10^{-5}	400
5.6×10^{-4}	450
2.4×10^{-3}	500

The equilibrium has also been investigated by Vvedenskii, Vinnikova, and Frost (231a).

The equilibrium has recently been reinvestigated by Storch and Kassel (203a). They correct for the production of methane and propylene as described in section IIB, and thus obtain the values given in table 11A. These values are lower than those of Pease and Durgan, and of Frey and

TABLE 11A

The ethane-ethylene equilibrium at 565°C. (Storch and Kassel)

TIME	INITIAL PRESSURES		FINAL PRESSURES				K	
	C_2H_6	C_2H_4	H_2	C_nH_{2n}	C_3H_4	C_2H_6	Uncorrected for C_3H_6	Corrected for C_3H_6
min.	*mm.*	*mm.*	*mm.*	*mm.*	*mm.*	*mm.*	*atm*$^{-1}$	*atm.*$^{-1}$
60	1299 9	149 9	65 0	178 2	132 4	1215 8	0 0125	0 0093
60	616.8	75 4	41 6	107 7	95 1	571 9	0.0103	0 0091
60	716.3	0 0	64 7	64 9	58 7	642.8	0.0086	0 0078
60	1432 5	0 0	108 7	108 4	85 3	1306 0	0 0119	0 0093
120	1472 3	0 0	121 2	115 1	58 4	1295 5	0 0142	0 0072
120	377 5	0 0	53 6	49 8	42 7	318 1	0 0110	0 0095
Average.								0 0087

Huppke as recalculated by Kistiakowsky et al. However, Pease and Durgan determined ethylene by absorption with bromine water, and thus their "ethylene" was really $C_2H_4 + C_3H_6$. Storch and Kassel attempt to correct for this and get

$$K = 0.020 \quad \text{at } 600°C.$$

$$K = 0.052 \quad \text{at } 650°C.$$

These values are in good agreement with their own work. They are also in much better agreement with the calculations of Smith and Vaughan (187a) based on spectroscopic and thermochemical data.

Pease (142, 144) investigated the rate of the hydrogenation reaction.

[3] In the original paper, owing to a typographical error, these temperatures are given as °K. instead of °C.

He found that, in the main, the hydrogenation went smoothly to ethane, although a small amount of polymerization of ethylene occurred as well. The reaction was almost entirely homogeneous and of the second order. A steric factor of 0.1 was found, which is surprisingly high for an association reaction between comparatively simple molecules. The rate of the reaction was given by
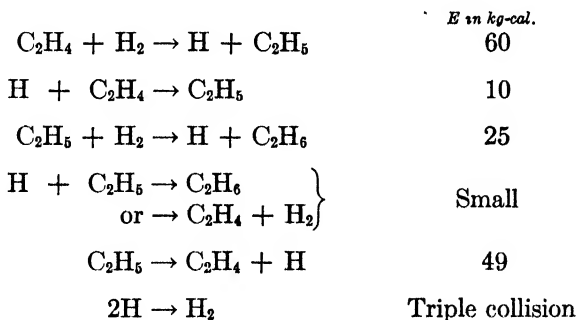
$$\log_{10} k = 5.576 - \frac{43,150}{2.3RT} \text{ liter mol.}^{-1} \text{ sec.}^{-1}$$

As mentioned before, combination of this result with Marek and McCluer's data for the reverse reaction gives calculated equilibrium constants in excellent agreement with those found by Pease and Durgan. A few experiments on the hydrogenation of ethylene were also made by Frey and Smith (59).

Pease and Wheeler (149, 232) compared the rates of hydrogenation of ethylene with hydrogen and with deuterium. For the homogeneous reaction at 500°C. they found that the reaction with hydrogen was the faster by a factor of 2.5. This is about what one would expect on the basis of the difference in zero-point energies and collision frequencies.

3. Free radicals and the reactions of ethylene

Rice and Herzfeld (162) have suggested a free-radical mechanism for the ethylene hydrogenation, viz.,

	E in kg-cal.
$C_2H_4 + H_2 \rightarrow H + C_2H_5$	60
$H + C_2H_4 \rightarrow C_2H_5$	10
$C_2H_5 + H_2 \rightarrow H + C_2H_6$	25
$H + C_2H_5 \rightarrow C_2H_6$ or $\rightarrow C_2H_4 + H_2$	Small
$C_2H_5 \rightarrow C_2H_4 + H$	49
$2H \rightarrow H_2$	Triple collision

This leads to good agreement with experiment, but in view of the criticisms which have already been raised against the Rice–Herzfeld mechanism for the reverse reaction (the ethane decomposition) it seems very unlikely that the above scheme holds. In any case, the activation energies assigned to the individual steps are in need of revision.

There is abundant evidence, on the other hand, that ethylene is affected by the addition of free radicals.

In the course of an investigation of the oxidation of ethylene, Lenher

(108) found that the substance polymerizes much faster in the presence of oxygen than it does alone. Thus from 1 to 5 per cent polymerized in 3 sec. at temperatures from 480° to 600°C. in the presence of 0.5 to 0.7 per cent oxygen. The product was propylene, together with a small amount of butylene. Lenher concluded that the only reasonable assumption was that in the presence of oxygen we have

$$C_2H_4 \rightarrow 2CH_2$$

$$C_2H_4 + CH_2 \rightarrow C_3H_6$$
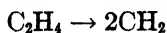
the dissociation into methylene radicals perhaps occurring through the intermediate formation and decomposition of a peroxide.

Taylor and Jones (207, 215) made the first experiments on a reaction sensitized by free radicals, following a suggestion made by Taylor (206) in 1925. They decomposed mercury and lead alkyls in a hydrogen-ethylene mixture, and found that there was some hydrogenation, but that the main result was polymerization of the ethylene. The reaction was shown to be independent of surface effects. They suggested that the mechanism was

$$Hg(C_2H_5)_2 \rightarrow Hg + 2C_2H_5$$

$$C_2H_5 + C_2H_4 (+ M) \rightarrow C_4H_9 (+ M), \text{ etc.}$$
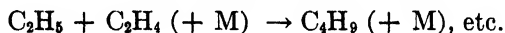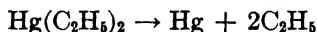
followed by the disappearance of the radicals by reactions of the type

$$C_nH_{2n+1} + C_2H_5 \rightarrow C_2H_6 + C_nH_{2n}$$

$$C_nH_{2n+1} + C_2H_4 \rightarrow C_2H_5 + C_nH_{2n}$$
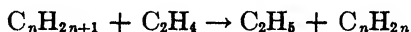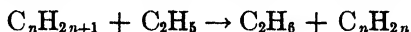
They pointed out the striking parallelism between these results and those of Taylor and Hill on the mercury-photosensitized reaction (q. v.).

Rice and Sickman (170, 185) found that ethylene was polymerized in the presence of decomposing azomethane at 300°C. They used a wide range of partial pressures of both substances and found that the initial rate of polymerization was proportional to

$$[\text{azomethane}]^{\frac{1}{2}} [C_2H_4]^{\frac{3}{2}}$$

Pressure–time curves of the ordinary shape were obtained, instead of the autocatalytic type usually found in thermal polymerizations. The average values of the velocity constants were

$$k_{310°} = 6.5 \times 10^{-6} \text{ mm.}^{-1} \text{ sec.}^{-1}$$

$$k_{290°} = 3.0 \times 10^{-6} \text{ mm.}^{-1} \text{ sec.}^{-1}$$

4. The photodecomposition of ethylene

Early investigations did not distinguish very clearly between the direct photochemical reactions of ethylene and the mercury-photosensitized reaction.

The first definite information on the direct photoreaction was obtained by Mooney and Ludlam (127). They found that ethylene did not absorb light of wave length greater than 2130 A.U. to any appreciable extent, and concluded that nothing was to be expected from investigations with a mercury arc source (provided that mercury vapor is kept out of the reaction vessel, otherwise, of course, the mercury-photosensitized reaction will come into play). Mooney and Ludlam used as source an aluminum spark with a high intensity at 1860 A.U. and found that acetylene was formed. They suggested that the mechanism was perhaps

$$C_2H_4 \rightarrow C_2H_2 + 2H$$

Qualitative observations by Lind and Livingston (112) are in agreement with these results. Taylor and Emeleus (211, 212), however, showed that a mercury arc did cause appreciable polymerization of ethylene, and they concluded that this was to be ascribed to absorption by ethylene of wave lengths near the limit of transmission of silica.

Recently McDonald and Norrish (116) have reinvestigated the reaction, using a hydrogen lamp source and a fluorite apparatus. They were thus able to work with light of shorter wave lengths. Hydrogen, a polymer, and a condensable gas were formed under these conditions. Spectroscopic observations suggest (71, 151, 152) that the primary process is

$$C_2H_4 \rightarrow 2CH_2$$
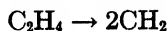
If this is so, the polymerization is easily explained as due to

$$C_2H_4 + CH_2 \rightarrow C_3H_6, \text{ etc.}$$
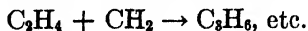
The formation of hydrogen is hard to explain, however, since on this basis it could only arise by

$$2CH_2 \rightarrow C_2H_2 + H_2$$

and this reaction would be very unlikely on account of the small concentration of methylene radicals. As an alternative explanation they suggest

$$C_2H_4 \rightarrow C_2H_2 + 2H$$

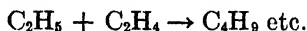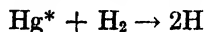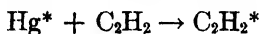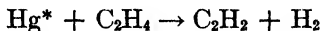together with

$$C_2H_4 \rightarrow C_2H_2 + H_2$$

followed by secondary reactions of hydrogen atoms to yield ethane and butane. Further work is promised from Norrish's laboratory.

5. The mercury-photosensitized reactions of ethylene

The first investigation of this kind was that of Berthelot and Gaudechon (12), who found that an oily polymer was formed, with no gaseous products. Landau (103) similarly found that on long exposure to a mercury arc ethylene (in the presence of mercury vapor) could be completely polymerized to condensable products.

The first quantitative measurements were made by Taylor and Bates (4, 209), using a cooled mercury arc. They found that polymerization occurred, together with the formation of acetylene, hydrogen, and some methane. They point out that a great many different reactions are possible in such a system. Thus, for example,

$$Hg^* + C_2H_4 \rightarrow C_2H_2 + H_2$$

$$Hg^* + C_2H_2 \rightarrow C_2H_2^*$$

$$C_2H_2^* + nC_2H_2 \rightarrow \text{cuprene}$$

$$Hg^* + H_2 \rightarrow 2H$$

$$H + C_2H_4 \rightarrow C_2H_5$$

$$C_2H_5 + C_2H_4 \rightarrow C_4H_9 \text{ etc.}$$

It also follows that it is impossible to treat the polymerization reaction and the reaction of ethylene with hydrogen atoms entirely separately.

The polymerization was also investigated in a similar way by Olson and Meyers (133) and by Taylor and Hill (214). A brief investigation was also made by Melville (125), who found acetylene, hydrogen, and condensable products, in agreement with other investigators. He adopts the primary step suggested by Taylor and Bates, and ascribes all further changes to secondary reactions of acetylene. There is no doubt that the processes occurring are far too complicated to be disentangled at present.

Taylor and Bates (5, 208) have also shown that ethylene can be polymerized by cadmium photosensitization, using the resonance line at 3262 A.U. as a source. This corresponds to a much smaller quantum than in the mercury-photosensitized reaction, viz., 87,000 cal. Jungers and Taylor (81) attempted to investigate the sodium-photosensitized reaction, using a commercial sodium lamp as a source (the sodium D line corresponds to 48 kg-cal.). They found that ethylene quenched the resonance, but that no polymerization occurred.

6. The reaction of ethylene with hydrogen atoms

This reaction has been investigated by the Wood–Bonhoeffer method by von Wartenberg and Schultze (231). They found that chemilumi-

nescence occurred, the emitted light corresponding to the C—C and C—H bands, and that the reaction was rapid and yielded principally ethane, with a little acetylene. Geib and Harteck (62) found that ethane was also formed when ethylene and hydrogen atoms were brought together at liquid-air temperature.

By mercury photosensitization the reaction was first investigated in a qualitative way by Taylor and Marshall (216), using a cooled mercury arc as a source. They found that there was a steady drop in pressure, presumably owing to the formation of ethane. With a hot arc (in which the resonance line is reversed) there was no reaction, showing that the primary process was

$$Hg^* + H_2 \rightarrow 2H$$
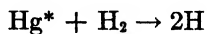
The rate was very high for the intensity of the light used, suggesting a chain reaction.

Olson and Meyers (133) also investigated the reaction by the same method. They found that the drop in pressure was not quite that corresponding to the reaction

$$C_2H_4 + H_2 \rightarrow C_2H_6$$

perhaps owing to the formation of some methane. In a later paper (133a) they showed by mass-spectrographic analysis that methane, ethane, propane, and butane were formed. When hydrogen and ethylene were present in about equal quantities, considerable higher hydrocarbons were formed and very little methane. Thus with initial pressures of 39 cm. of hydrogen and 25 cm. of ethylene the relative amounts of the products were as follows: $CH_4 = 0.018$; $C_2H_6 = 1$; $C_3H_8 = 0.64$; $C_4H_{10} = 0.42$. If, however, hydrogen was in large excess the situation was reversed and very little propane and butane were formed. For example with 40 cm. of hydrogen and 2 cm. of ethylene they found the following relative amounts: $CH_4 = 0.22$; $C_2H_6 = 1$; $C_3H_8 = 0.04$; $C_4H_{10} = 0.0008$. They conclude that three primary processes occur,

$$Hg^* + H_2 \rightarrow 2H$$

$$Hg^* + C_2H_4 \rightarrow C_2H_2 + H_2$$

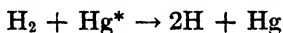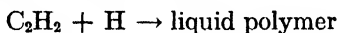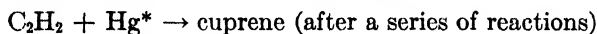$$Hg^* + C_2H_4 \rightarrow 2CH_2$$
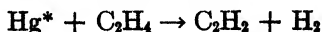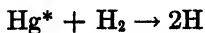
Bates and Taylor (4) also found that some polymerization accompanied the formation of ethane. The occurrence of the reaction was also noted by Hirst (74).

By far the most thorough investigation is that of Taylor and Hill (213, 214). They found that when hydrogen was in large excess the products

were practically exclusively ethane, but with relatively more ethylene higher hydrocarbons were formed (average C_4) including a liquid of molecular weight about 230. Some methane was also formed. There is thus fairly good general agreement between the work of Taylor and Hill and that of Olson and Meyers. Since the products of higher molecular weight react faster than those of lower, the process becomes extremely complicated once higher products have started to form, and the liquid product presumably results from secondary reactions of saturated hydrocarbons. (Compare with the photosensitized reactions of ethane, for example.) With a very large excess of ethylene some acetylene is formed.

Taylor and Hill conclude that the apparently simple results of von Wartenberg and Schultze were due to the low pressure and large excess of hydrogen used in their experiments. They discuss the possible reaction steps in some detail, and conclude that the main reactions are

$$C_2H_4 + Hg^* \rightarrow C_2H_2 + H_2 + Hg$$

$$C_2H_2 + Hg^* \rightarrow \text{cuprene (after a series of reactions)}$$

$$C_2H_2 + H \rightarrow \text{liquid polymer}$$

$$H_2 + Hg^* \rightarrow 2H + Hg$$

$$C_2H_4 + H_2 + M \rightarrow C_2H_6 + M$$

$$C_2H_4 + H + M \rightarrow C_2H_5 + M$$

together with various reactions of radicals, etc., leading to the formation of products of higher molecular weight.

The reaction has also been investigated by Klemenc and Patat (96). They agree with Taylor and Hill in general, but consider that the hydrogenation process is never as smooth as found by them, and is always accompanied by some polymerization. The polymerization process is complicated, but they suggest that it occurs mainly by the preliminary formation of acetylene and hydrogen, followed by polymerization of the acetylene as suggested by Taylor and Hill.

Melville (124) compared the reactions of ethylene with hydrogen and with deuterium atoms. He found no detectable difference in rate, and therefore concludes that the rate-controlling step must be hydrogen-atom or a deuterium-atom reaction, since otherwise the difference in zero-point energies would make itself felt.

Taylor and Emeleus (210) have shown that the ethylene polymerization can be photosensitized by ammonia, presumably owing to hydrogen atoms or to radicals from the ammonia decomposition. Similar results were obtained using methylamine and ethylamine (212).

In a recent paper Taylor and Jungers (215a) report an investigation of the acetone-photosensitized polymerization of ethylene over a wide range

of temperature. There is no doubt (132a) that the primary step is the photodissociation of acetone to yield free methyl radicals, which then induce polymerization of the ethylene. Taylor and Jungers find that the polymerization occurs readily at room temperature, and that the temperature coefficient of the reaction is very small. The maximum effect found was the polymerization of eleven ethylene molecules per methyl radical, assuming two methyl radicals from each decomposing acetone molecule. They conclude that the relatively high activation energy (35 to 42 kg-cal.) of the thermal polymerization process is the activation energy of the primary step, possibly involving the formation of a free radical. Once free radicals are produced, it appears that subsequent polymerization reactions proceed with a low energy of activation.

B. Propylene

Frey and Smith (59) investigated the thermal decomposition of propylene at one temperature only, but made very thorough analyses of the products of the reaction. At 575°C., an initial pressure of 1 atm., and a contact time of 4 min., they obtained the following results:

PRODUCT	PER CENT	PRODUCT	PER CENT
N_2	0.4	C_3H_6	68.9
H_2	1.7	C_3H_8	3.0
CH_4	10.7	C_4H_8	2.8
C_2H_4	8.0	C_5 to C_8	2.6
C_2H_6	1.9	Higher hydrocarbons	0.0

It will be seen that at these high temperatures the reaction is mainly decomposition rather than polymerization. Assuming the reaction to be of the first order, the above results give a velocity constant for the reaction of about 0.0012 sec.$^{-1}$ This is about 10 per cent faster than the decomposition of ethylene under the same conditions.

The reaction has recently been investigated by Moor, Strigaleva, and Frost (127b) by a flow method. They worked at atmospheric pressure, and at temperatures from 610° to 726°C. The products of the reaction were roughly as follows:

PRODUCTS	MOLES PER 100 MOLES OF PROPYLENE REACTING	
	At 610 to 644°C.	At 644 to 726°C.
C_5 and higher hydrocarbons	60	50
Saturated hydrocarbons (chiefly methane)	20	30
C_2H_4	40	50
H_2	15	15

The reaction was neither of the first nor of the second order, the calculated first-order constants increasing rapidly with increasing percentage conversion. This is probably due to the fact that the primary step is of the first order, but that there are many complicating secondary processes.

A qualitative investigation of the reaction has also been made by Mitsengendler (126a).

The polymerization reaction at lower temperatures has been investigated by Krauze, Nemtzov, and Soskina (99, 101). The reaction is found to be mainly

$$2C_3H_6 \rightarrow C_6H_{12}$$
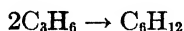
and the rate can be expressed by the equation

$$\log_{10} k = 10.2 - \frac{37,400}{2.3RT} \text{ liter mol.}^{-1} \text{ sec.}^{-1}$$

Frey and Smith (59) have also reported a few experiments on the "hydrogenation" of propylene at 575°C. and 1 atm. pressure. The results are given in table 12. It will be seen that the reaction is still mainly decomposition and polymerization, and that little real hydrogenation occurs at this temperature.

C. The higher olefins

Egloff and Parrish (43) point out that the activation energies of the polymerization reactions of the olefins are about 38 to 40 kg-cal. This is much less than the energy required to break bonds, and hence the polymerization reactions predominate at lower temperatures for all the olefins. For comparative purposes the "temperatures of initial decomposition" are of interest. The temperature of initial decomposition is arbitrarily defined at the temperature at which a noticeable amount of decomposition will just occur in six hours. Some typical values are given in table 13, and are compared with the values for the corresponding saturated hydrocarbons.

Most of our knowledge of the polymerization reactions of the higher olefins comes from the work of Krauze, Nemtzov, and Soskina, who have investigated the polymerization at high pressures of ethylene (98, 100), propylene (99, 101), the butylenes, and amylene (99, 102) in the temperature range 300° to 400°C. The reactions are all of the second order, the products being mainly but not exclusively those corresponding to a straight association to give an olefin with twice the number of carbon atoms. The rate of polymerization falls off slightly with increasing molecular weight. The kinetic constants are summarized in table 14.

With the exception of the values for isobutylene, it will be seen that A

and E are almost the same for all members of the series.   The difference in the case of isobutylene is of considerable interest, if real.   However, the fact that both A and E alter in such a way as to compensate for one

TABLE 12

The "hydrogenation" of propylene at 575°C. and 1 atm. (Frey and Smith)

SUBSTANCE	TIME				
	0 min	1 min.	2 min	4 min.	6 min
N_2	0 7	0.5	0.6	0.7	1.0
H_2	54.7	53.0	49 4	48 4	49.9
CH_4	0.0	1.8	4 2	7.5	9.4
C_2H_4	0.3	1 6	2 7	5.2	6 1
C_2H_6		0 4	1 2	1 7	1 9
C_3H_6	43.7	40 1	37 7	31 3	25.0
C_3H_8	0 6	1 2	1.8	3.0	4 3
Higher hydrocarbons	0 0	1 4	2.4	2 4	2.4

TABLE 13

Temperatures of initial decomposition of hydrocarbons (Egloff and Parrish)

HYDROCARBON	TEMPER-ATURE	HYDROCARBON	TEMPER-ATURE
	°C.		°C.
Ethylene	380	Methane	540
Propylene	357	Ethane	450
2-Butene	350	Propane	425
1-Butene	325	n-Butane	400
1- or 2-Pentene	390 (?)	n-Pentane	391

TABLE 14

The polymerization of the olefins (Krauze et al)

REACTION	E	$\log_{10}A$	COLLISION EFFICIENCY
	cal.		
$2C_2H_4 \rightarrow C_4H_8$	37,700⎫*	10.8	4×10^{-3}
$2C_3H_6 \rightarrow C_6H_{12}$	37,400⎭	10 2	1×10^{-3}
$2C_4H_8 \rightarrow C_8H_{16}$	38,000	10.0	5×10^{-4}
$2\,iso\text{-}C_4H_8 \rightarrow C_8H_{16}$	43,000†	12.3	1×10^{-1}
$2C_5H_{10} \rightarrow C_{10}H_{20}$	38,000	9.8	4×10^{-4}

* In a later paper (102) the activation energies of these reactions are given as 38,400 and 38,000 cal., respectively.

† The equilibrium in this reaction has been investigated at high pressures by Dobronravov and Frost (34a) who found

$$\log_{10} P_{C_4H_8}^2 / P_{C_8H_{16}} = \frac{2959}{T} + 6.049$$

another makes the result somewhat open to suspicion. The difference between the values for isobutylene and the others can be shown in another way. Bawn (6) has calculated the collision efficiencies of all the above reactions (i.e., the ratio of the number of molecules reacting to the number possessing the energy of activation, as calculated from the kinetic theory). His results are given in the last column of table 14, and it seems very unlikely that there should be such a great difference between the two butylenes, although it is worthy of note that the rather uncertain results on the decomposition of n-butane and isobutane (q.v.) are also widely different. Of course, none of these reactions is entirely simple, and in every case some of the primary products are polymerized further. It may well be that some such secondary process is the cause of the discrepancy. In any case the results are of very definite interest, and the reactions of the two butylenes would be well worth reinvestigation.

The decomposition at higher temperatures of pentene-2 was investigated by Pease and Morton (148), but not very thoroughly. They found that the reaction was definitely homogeneous and unimolecular, the pressure increase accompanying it was almost exactly 100 per cent, and the pressure–time curve was very regular. The products of the reaction corresponded to

$$CH_3CH_2CH{=}CHCH_3 \rightarrow CH_4 + CH_2{=}CH{-}CH{=}CH_2$$

$$CH_3CH_2CH{=}CHCH_3 \rightarrow C_2H_4 + C_3H_6$$

together with some formation of $CH_3CH_2CH{=}CH_2$. The rate was given by the equation

$$\log_{10} k = 13.33 - \frac{61,000}{2.3RT} \text{ sec.}^{-1}$$

The high-temperature decomposition of butene-2 has been investigated by Moor, Frost, and Shilyaeva (127a). The reaction has no simple order, presumably owing to complications due to secondary processes. A complicated set of products is obtained.

The homogeneous thermal isomerization of butene-2 was investigated by Kistiakowsky and Smith (95). The reaction is complex and the results are difficult to interpret, probably owing to chain processes.

The equilibrium in the reaction

$$n\text{-butene} \rightleftarrows \text{isobutene}$$
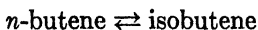
has been investigated by Serebryakova and Frost (183a).

Frey and Huppke (58b) have investigated the equilibria in a number of olefin hydrogenation reactions. Their results are summarized in table

14A, and equilibrium constants for a few temperatures are given in table 14B. These results and others have recently been reviewed by Parks (134b). Thermodynamic data for the olefins have been summarized by Thomas, Egloff, and Morrell (218a), and thermochemical data by Rossini (172a) and Rossini and Knowlton (172b).

The only other kinetic investigations of importance are those of Vaughan (228, 229), who found that the polymerizations of isoprene and of buta-

TABLE 14A

Equilibria in a number of olefin hydrogenation reactions

REACTION	VALUES OF ΔF	VALUES OF $\Delta F_{400°C.}$
		calories
$C_2H_6 \rightleftarrows C_2H_4 + H_2$	$\Delta F = 27,798 - 9.21T \log_{10} T + 2.17T$	11,730
$C_3H_8 \rightleftarrows C_3H_6 + H_2$	$\Delta F = 25,920 - 9.21T \log_{10} T - 0.21T$	8,250
$n\text{-}C_4H_{10} \rightleftarrows C_2H_5CH=CH_2 + H_2$	$\Delta F = 25,790 - 9.21T \log_{10} T - 0.21T$	8,120
$n\text{-}C_4H_{10} \rightleftarrows cis\text{-}CH_3CH=CH\text{-}CH_3 + H_2$	$\Delta F = 25,580 - 9.21T \log_{10} T - 0.21T$	7,910
$n\text{-}C_4H_{10} \rightleftarrows trans\text{-}CH_3CH=CH\text{-}CH_3 + H_2$	$\Delta F = 25,090 - 9 21T \log_{10} T - 0.21T$	7,420
$iso\text{-}C_4H_{10} \rightleftarrows (CH_3)_2C=CH_2 + H_2$	$\Delta F = 23,900 - 9.21T \log_{10} T - 0.21T$	6,230

TABLE 14B

Equilibrium constants for dehydrogenation reactions of paraffins (Frey and Huppke)

	EQUILIBRIUM CONSTANT			
	350°C.	400°C.	450°C.	500°C.
	atm.$^{-1}$	*atm.$^{-1}$*	*atm.$^{-1}$*	*atm.$^{-1}$*
$C_2H_6 \rightleftarrows C_2H_4 + H_2$		0.00015	0.00076	0.0032
$C_3H_8 \rightleftarrows C_3H_6 + H_2$	0.00038	0 0022	0.0074	
$n\text{-}C_4H_{10} \rightleftarrows C_2H_5CH=CH_2 + H_2$	0.00045	0.0022	0.0075	
$n\text{-}C_4H_{10} \rightleftarrows cis\text{-}CH_3CH=CHCH_3 + H_2$	0.00083	0.0039	0.014	
$n\text{-}C_4H_{10} \rightleftarrows trans\text{-}CH_3CH=CHCH_3 + H_2$	0 00052	0.0025	0.0087	
$iso\text{-}C_4H_{10} \rightleftarrows (CH_3)_2C=CH_2 + H_2$	0 0017	0.010	0 042	

diene were homogeneous second-order reactions. For 1,3-butadiene his results are given by

$$\log_{10} k = 7.673 - \frac{24,700}{2.3RT} \text{ liter mol.}^{-1} \text{ sec.}^{-1}$$

The steric factor is small, corresponding to a collision efficiency of 1/10,300, as might be expected for an association reaction. The reaction has also

been investigated by Moor, Strigaleva, and Shilyaeva (128), results similar to those of Vaughan being obtained. For isoprene Vaughan found a rate given by

$$k = 2.19 \times 10^{10} \, T^{\frac{1}{2}} \, e^{-28,900/RT} \text{ liter mol.}^{-1} \text{ sec.}^{-1}$$

with a steric factor of about 1/530.

Lind and Livingston (112) have investigated the photopolymerization of allene. They find the quantum yield to be about 2.5, independent of the pressure and the light intensity. The light absorption commences below 2380 A.U. and is strong below 2300 A U. They also studied the photopolymerization of isoprene in a qualitative way.

<div align="center">IV. ACETYLENIC HYDROCARBONS</div>

It will be apparent from the preceding sections that our knowledge of the reactions of the olefins is in a much less satisfactory state than is that of the paraffins. On account of the complexity of the reactions, the unsatisfactory state of our knowledge is still more pronounced in the case of the acetylenic hydrocarbons, and little is known with certainty about the elementary processes.

<div align="center">

A. Acetylene

1. The thermal decomposition and polymerization

</div>

No attempt will be made to review the enormous literature on the effect of heat on acetylene, since comprehensive discussions from a pyrolytic point of view already exist (40, 42). The products of the reactions are usually so complicated as to defy analysis; consequently very little is known which is of value from the standpoint of this review. We shall therefore discuss only those papers which seem to bear on the main features of the processes.

At low temperatures (below 600°C.) polymerization is almost the only reaction of acetylene, the products being either a yellow solid, probably cuprene, or a liquid of aromatic character. From 600° to 1000°C. polymerization and decomposition both occur, the decomposition products being carbon, hydrogen, and some methane. Above 1000°C. decomposition is the only reaction of importance, and the decomposition is complete at 1200° to 1300°C. (10). At still higher temperatures some acetylene exists in equilibrium with hydrogen, carbon, and methane (18, 153, 154).
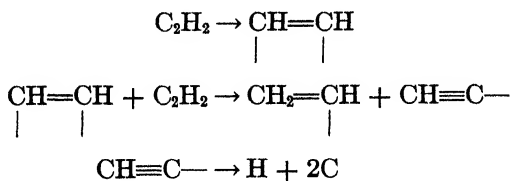
Although a very large number of papers have been published on the high-temperature decomposition of acetylene, very little is known about the kinetics of the process, and little can be added to the information derived from the early work of Bone and his collaborators. Bone and

Coward (16, 17) found that at 800°C. and higher acetylene always "flashed" on being admitted to the reaction vessel unless largely diluted with nitrogen or hydrogen. This explosive characteristic, due to the exothermic nature of the reaction, prevents any accurate determination of the rate of the reaction under isothermal conditions. The pressure and temperature limits at which explosion occurs have been determined by Schlapfer and Brunner (180). Bone and Coward found that a certain amount of polymerization accompanied the decomposition during the "flashing." The products, apart from carbon, were mainly methane and hydrogen. At still higher temperatures polymerization decreased, and the reaction became a practically straight decomposition as shown by table 15. Bone and Jerdan (19) found that at 1150°C. decomposition was 90 per cent complete in 1 min. Methane was formed in large quantities in the early stages of the process, and was later partially decomposed.

While a great deal of further work has been done on the production of various compounds from acetylene by pyrolysis, it cannot be said that much is known about the mechanism of the process. The original mechanism proposed by Bone and Coward for the decomposition was a split into radicals

$$C_2H_2 \rightarrow 2CH$$
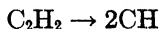
which later recombined or were hydrogenated to give methane and other products. It is now known that such a primary step would be impossibly endothermic. Hurd (78) suggests that the primary step involves the rupture of only one bond,

$$C_2H_2 \rightarrow \underset{|}{CH}=\underset{|}{CH}$$

$$\underset{|\quad|}{CH}=\underset{}{CH} + C_2H_2 \rightarrow CH_2=\underset{|}{CH} + CH\equiv C—$$

$$CH\equiv C— \rightarrow H + 2C$$

This type of mechanism was originally suggested by Mecke (123) and Bodenstein (14), and is, of course, purely speculative. The mechanism has also been discussed by Egloff and Wilson (48).

Rather more information is available concerning the polymerization which occurs at lower temperatures. The first data of any kinetic significance were obtained by Pease (141), using a flow method. He found that at low temperatures the reaction was almost entirely polymerization, very little permanent gases (hydrogen, methane, and olefins) being formed at temperatures below 550° to 600°C. The liquid polymerization products were a complex mixture. Pease suggests that the primary product is

$(C_2H_2)_4$. Zelinski (237), on the other hand, found diacetylene to be a product, and suggested that the primary step was

$$2C_2H_2 \rightarrow (C_2H_2)_2$$
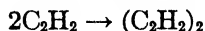
The reaction appears to be homogeneous, the rate being reduced to about one-half on packing the reaction vessel. Pease suggests that this is due to improved dissipation of heat in the packed vessel. (The polymerization is highly exothermic; thus for the reaction $3C_2H_2 \rightarrow C_6H_6$ there is an evolution of about 150 kg-cal. per mole.) Pease found that the reaction was roughly bimolecular, although he did not make a very thorough investigation of the order of the reaction. The bimolecular velocity constants for experiments at 1 atm. pressure are given in table 16.

TABLE 15

The thermal reactions of acetylene (Bone and Coward)

Temperature	600°C.	1000°C.	1150°C.
Polymerization (per cent of acetylene consumed) ..	19	7.5	5

GASEOUS PRODUCTS	MOLE PER CENT		
Acetylene . . .	1 35	1.55	0 0
Ethylene	0.45	2.60	0 0
Ethane	0 50	0.0	0 0
Methane	32.40	36.00	23 45
Hydrogen ..	63 50	59.85	76 55

The reaction was also investigated by the static method in a rather sketchy way by Schlapfer and Brunner (180). They found it to be homogeneous in Pyrex and quartz, a one hundred-fold increase in surface having no effect. They state that the results of analyses show that the reaction can be accurately followed by the pressure change; no analytical results are given, but presumably they followed the reaction by analyzing for unchanged acetylene. The products are complex, the average molecular weight being higher at low temperatures than at high. No data of any kind are given except for one run at 420°C., the results of which are given in table 17. It will be seen that the velocity constants fall when calculated for a first-order reaction, and rise when calculated for a second-order change. The real order is evidently about 1.5 for this experiment, but it is impossible to place much confidence in the results of a single run. For this run neither the initial pressure nor the units in which the velocity constants are expressed are given. The unimolecular constants are obviously in min.$^{-1}$, and the bimolecular constants are presumably expressed in liter mol.$^{-1}$ sec.$^{-1}$. If these assumptions are correct, their rates are very much faster than those of other observers.

A more thorough investigation was made by H. A. Taylor and van Hook (205), who also employed the static method. They followed the reaction by pressure change and obtained very reproducible results provided that the reaction vessel was aged for one or two runs. They found that an end point was reached when the pressure had decreased to 0.325 of its original value. No analyses of any kind were reported, but in view of Schläpfer and Brunner's statement it is probably safe to assume that the pressure change is a reliable measure of the extent of reaction. Taylor and van

TABLE 16

The thermal polymerization of acetylene (Pease)

TEMPERATURE	BIMOLECULAR VELOCITY CONSTANTS FOR EXPERIMENTS AT 1 ATM.
°C.	*liter mol* $^{-1}$ *sec.*$^{-1}$
450	0.00018-0 00022
475	0 00034-0.00050
500	0 0011 -0.0015
525	0.0030 -0.0045
550	0.0050 -0.011
575	0.0099 -0.023
600	0.024 -0 033

TABLE 17

The polymerization of acetylene at 420°C. (Schläpfer and Brunner)

TIME	PER CENT REACTED	$k_{unimol.}$	k_{bimol}
min.			
30	13.8		0 0054
60	27.8	0 0059	0.0065
120	47.2	0 0052	0 0074
180	56.2	0.0043	0 0071
300	71.5	0.0036	0.0084

Hook accept Pease's suggestion that the primary product is $(C_2H_2)_4$, and assume that some accompanying 'decomposition accounts for the final pressure being 0.325 of the initial pressure rather than 0.25. The reaction is apparently bimolecular in the early stages, but the constants deviate later. No test of the homogeneity of the reaction was made. Taylor and van Hook's velocity constants are compared with those of other workers in table 18. It will be seen that their rates are greater than those of Pease by a factor of about 2. Their results lead to an activation energy of 40,500 cal., but since no attempt was made to sort out the decomposition and the polymerization reactions this value is probably not very accurate.

On the basis of this activation energy they calculate a collision efficiency of
$\frac{1}{5}$. They conclude that the simplicity of the molecule is responsible for the
surprisingly high collision efficiency for an association reaction of this type
(compare the polymerization reactions of the olefins). Actually one would
expect a lower efficiency the simpler the molecule. It seems probable that
complications due to the presence of the simultaneous decomposition
reaction are responsible for the high apparent collision efficiency.

TABLE 18

The polymerization of acetylene (Taylor and van Hook)

TEMPERATURE	k	OBSERVER
°C.	liter mol.$^{-1}$ sec.$^{-1}$	
420	0 005–0 008	Schlapfer and Brunner
495	0 0039	Taylor and van Hook
500	0.0011–0 0015	Pease
515	0.0078	Taylor and van Hook
525	0.0030–0.0045	Pease
535	0 0145	Taylor and van Hook
550	0 0049–0.011	Pease

Travers (224) also gives the results of two experiments on the poly-
merization of acetylene. These do not contribute anything new to the
situation.

2. The thermal hydrogenation of acetylene

The thermal hydrogenation of acetylene was also investigated by Taylor
and van Hook. The actual hydrogenation is difficult to disentangle, since
decomposition and polymerization are both occurring at a much faster
rate than the hydrogenation. Taylor and van Hook attempted to sepa-
rate the effect of the hydrogenation reaction from that of the others on
the basis of the pressure change alone, without analyses of any kind. The
results are therefore highly speculative. The velocity constants thus
derived are as follows:

TEMPERATURE	$k_{\text{hydrogenation}}$
°C.	liter mol.$^{-1}$ sec.$^{-1}$
495	0.00019
505	0.00028
515	0.00039
525	0.00055
535	0.00076

These lead to an activation energy of 42,000 cal. Taylor and van Hook calculate a collision efficiency for the reaction

$$C_2H_2 + H_2 \rightarrow C_2H_4$$

of $\frac{1}{3}$, as in the case of the polymerization. In these calculations they use the surprising value of 1×10^{-8} cm. for the diameter of the hydrogen molecule. The collision efficiency is again unexpectedly high for an association reaction involving simple molecules. It seems probable that the activation energies of both reactions are somewhat in error, the true values being lower than those given, and hence the collision efficiencies are also smaller. In any case, the existing data on both reactions are far from final.

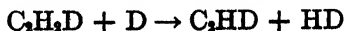### 3. The reaction of hydrogen atoms with acetylene

The reaction of hydrogen atoms with acetylene was investigated by Bonhoeffer and Harteck (23), and by von Wartenberg and Schultze (231). In the presence of acetylene it is found that the recombination of hydrogen atoms is strongly catalyzed, heat is given out, and there is a strong emission of light corresponding to the CH and C_2 bands. However, practically all the acetylene is recovered unchanged, so that presumably a series of reactions occur which consume hydrogen atoms and eventually regenerate acetylene. That such is the case is proved by an investigation of the reaction of acetylene with deuterium atoms by Geib and Steacie (64, 65). It was found that the acetylene recovered after the reaction was almost completely exchanged to deuteroacetylene. Apparently, then, the acetylene must be alternately hydrogenated and dehydrogenated. The reaction occurs so quickly that three-body processes are ruled out. Also, we can eliminate a mechanism of the type

$$C_2H_2 + D \rightarrow C_2H + HD \qquad (1)$$
$$C_2H + D_2 \rightarrow C_2HD + H \qquad (2)$$

both on energetic grounds, and because the atoms removed from the system by reaction 1 would be regenerated by reaction 2 and no "catalytic" recombination would occur. The mechanism, therefore, must be analogous to that previously discussed in the case of ethane, viz.,

$$C_2H_2 + D \rightarrow C_2H + HD$$
$$C_2H + D \rightarrow C_2HD$$
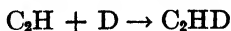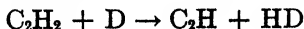
It is also possible that the exchange occurs through the formation of a quasi-molecule, C_2H_2D, i.e.,

$$C_2H_2 + D \rightarrow C_2H_2D$$
$$C_2H_2D + D \rightarrow C_2HD + HD$$

However, if the quasi-molecule had a long enough life to make such a mechanism possible, we would also expect the reaction

$$D + C_2H_2D \rightarrow C_2H_2D_2$$

to occur, and actually no appreciable quantity of ethylene is formed. As von Wartenberg and Schultze point out, the absence of hydrogenation to ethylene is somewhat surprising, since acetylene is very easily hydrogenated to ethylene by metal catalysts. Hydrogenation of acetylene to ethylene is also absent when the hydrogen atoms are produced by photosensitization with mercury (4).

Geib and Harteck (62) have also investigated the reaction of hydrogen atoms with acetylene at liquid-air temperature. They find that no addition compounds, stable or unstable, are formed.

4. Free radicals and acetylene

The possibility that the decomposition of acetylene involves free radicals is ruled out, since the two conceivable modes of decomposition into radicals

$$C_2H_2 \rightarrow 2CH$$

and

$$C_2H_2 \rightarrow C_2H + H$$
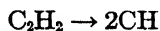
are so strongly endothermic that the activation energies would be far too high to permit their occurrence to an appreciable extent. As is to be expected, therefore, Paneth and Hofeditz (134) found that the products of the acetylene decomposition had no effect on metallic mirrors.

Little work has been done on the action of free radicals on acetylene. Sickman and O. K. Rice (185) found that methyl radicals from the azomethane decomposition caused the polymerization of acetylene. Further work on this reaction is promised, but has not yet appeared. Recently Taylor and Jungers (215a) have shown that acetylene can be polymerized by the action of methyl radicals produced by the photodecomposition of acetone. At 25°C. as many as five acetylene molecules were found to disappear per methyl radical.

5. The photopolymerization of acetylene

The earlier papers on the photopolymerization of acetylene served to establish the fact that such polymerization occurred, the main product being a yellow solid, "cuprene." Thenard (218) reported the formation of benzene as well, but this was not confirmed by Berthelot and Gaudechon (12) or by Reinicke (155). Bates and Taylor (4) also investigated the reaction in a qualitative but much more thorough manner and found cuprene and an "oil" as products. They point out that a large number of
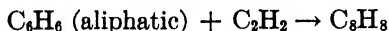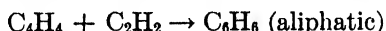
reactions are possible, particularly when the conditions are such that the photoreaction is accompanied by mercury-photosensitized reactions.

Lind and Livingston (110, 111) made the first really thorough investigation of the direct photoreaction, mercury vapor being excluded in order to avoid photosensitization. They showed that only light of wave length less than 2537 A.U. is effective (acetylene is transparent to longer wave lengths). The main cause of uncertainty in their work (and that of all other investigators) is the formation of an opaque solid deposit on the wall, which continually reduces the amount of light reaching the acetylene. They found that a solid resembling cuprene was formed, there being no gaseous products. The rate was proportional to the light intensity, and independent of the partial pressure of acetylene. The quantum yield for an average wave length of about 2150 A.U. was 9.2 ± 1.5.
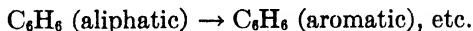
Kemula and Mrazek (93) investigated the reaction for the purpose of proving the presence or absence of benzene and gaseous products. They followed the reaction by absorption spectroscopy, so as to be able to detect transitory products. The results confirmed the work of Lind and Livingston in a general way, but showed that some benzene was formed in the reaction, together with small amounts of saturated hydrocarbons, olefins, and naphthalene derivatives. Kato (89) also found benzene to be a product. Kemula and Mrazek suggest that the primary reactions are

$$C_2H_2 + h\nu \rightarrow C_2H_2^*$$

$$C_2H_2^* + C_2H_2 \rightarrow C_4H_4 \text{ (vinylacetylene)}$$

Various secondary changes are then postulated, such as

$$C_4H_4 + C_2H_2 \rightarrow C_6H_6 \text{ (aliphatic)}$$

$$C_6H_6 \text{ (aliphatic)} + C_2H_2 \rightarrow C_8H_8$$

or

$$C_6H_6 \text{ (aliphatic)} \rightarrow C_6H_6 \text{ (aromatic), etc.}$$
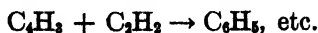
Criticisms of the work of Kemula and Mrazek by Toul (220, 221) seem to the writer to be entirely invalid, and have been satisfactorily answered by Kemula (91, 92).

Livingston and Schiflett (115) confirmed the results of Kemula and Mrazek, and found that benzene was formed in considerable quantities at temperatures above 270°C. Since the solid polymer found by Kemula and Mrazek had the approximate composition $(C_{10}H_9)_n$, Lind and Livingston (113) suggest the following mechanism for the photopolymerization:

$$C_2H_2 + h\nu \rightarrow C_2H_2^* \rightarrow C_2H + H$$

$$C_2H + C_2H_2 \rightarrow C_4H_3$$

$$C_4H_3 + C_2H_2 \rightarrow C_6H_5, \text{ etc.}$$

$$C_nH_{n-1} + C_mH_{m-1} \rightarrow \text{solid polymer } (n + m \text{ being about 20 so as to agree}$$
$$\text{with a quantum yield of about 10)}$$

They suggest that benzene may arise by

$$C_8H_7 \rightarrow C_6H_6 + C_2H$$

or

$$C_6H_5 + H \rightarrow C_6H_6$$

It must be admitted that at the moment all considerations as to mechanism are purely speculative, and nothing is known directly about any of the postulated part-reactions.

Toul (220) has also made a few rough qualitative experiments on the photodecomposition. He criticizes all previous work in a very drastic manner, owing to a lack of understanding on his part of photochemical and vacuum technique. He concludes that traces of "impurities" are largely responsible for the results obtained by others. His own technique, however, leaves much to be desired.

6. The mercury-photosensitized polymerization of acetylene

It was first shown that acetylene could be polymerized by mercury photosensitization by Bates and Taylor (4). A more thorough investigation was made by Melville (125, 171). He found that the rate was high at the start but fell off rapidly owing to the removal of mercury atoms by the polymerization process, presumably by the formation of a complex of some sort. If precautions were taken to ensure the presence of sufficient mercury vapor, the rate no longer fell off with time. All Melville's measurements were made at initial pressures below 10 mm., to prevent the formation of an opaque film on the walls of the reaction vessel. At low pressures (below 0.5 mm.) the rate was proportional to the acetylene pressure, because under these circumstances there is so little acetylene present that most excited mercury atoms radiate instead of being quenched. The quenching, therefore, does not appreciably lower the stationary concentration of excited mercury atoms, and hence the number of activated acetylene molecules produced is proportional to the acetylene pressure. At higher pressures the quenching lowers the concentration of excited mercury atoms to an appreciable extent, and the rate is proportional to $[C_2H_2]^x$, where x is less than 1 and approaches zero at high pressures.

The temperature was found to have a marked effect on the rate, viz.,

Temperature, °C.	30	99	209	267	355	436	528
Relative rate	1	8.8	12.7	9.0	7.5	6.2	5.3

It will be seen that the rate is a maximum in the neighborhood of 200–250°C. This is associated with the fact that the chain length is about 10

at room temperature, rises to about 100 at 250°C., and then decreases at higher temperatures. The chain length is independent of pressure, surface, or light intensity.

Melville gives a kinetic analysis of the polymerization process in terms of ordinary chain reaction theory, and concludes that the termination of the chains is by collision of the polymer with an acetylene molecule, the collision for some reason being not of the right type for propagation. The kinetic analysis is rather complex and will not be discussed here, since in the light of present knowledge it does not seem to be capable of either verification or disproof.

The polymerization was also investigated by Jungers and Taylor (80) for the principal purpose of comparing acetylene with deuterioacetylene. They found that at low pressures the rate for both C_2H_2 and C_2D_2 was proportional to the pressure, and that above 7 mm. it became independent of it. Over the whole pressure range the rate was 30 per cent greater for C_2H_2 than for C_2D_2. The quantum yield was found to be about 6.5 for ordinary acetylene and 5 for deuterioacetylene. (It is noteworthy that in the polymerization of acetylene by alpha particles (114) the rates for the two acetylenes are identical.) Taylor and Jungers compare the quantum yields and ion-pair yields for ordinary acetylene under different conditions:

	Quantum or ion-pair yield
For beta particles (Mund and Jungers (130)) . ..	26
For alpha particles (Lind and Bardwell (109), Mund and Koch (131))	18-20
For the photoreaction (Lind and Livingston (111))	9.2
For the mercury-photosensitized reaction (Jungers and Taylor (80))	6 5

It will be seen that the yield produced by each primary act falls off rapidly as the energy input in the primary act is diminished. Jungers and Taylor conclude, therefore, that the polymerization process must dissipate the initiation energy fairly rapidly as it progresses.

Heinemann (70) claims in an old patent that ultra-violet light forms propylene from a mixture of methane and acetylene. The validity of the statement appears doubtful.

B. Higher acetylenic hydrocarbons

No investigations worthy of mention exist, with the exception of a few observations on the photopolymerization of methylacetylene. The reaction was first studied in a purely qualitative way by Berthelot (11). It was later investigated somewhat briefly by Lind and Livingston (112), who found that light of wave length less than 2240 A.U. was effective.

The product of the reaction was a white solid polymer. The quantum yield is about 3.5, independent of pressure and light intensity.

V. CONCLUSION

In conclusion it may well be said that tremendous advances have been made in this field in the last few years. A great deal, however, remains to be done. More work is especially needed on the rôle of free radicals, elementary processes in general, the reactions of the higher olefins and acetylenic hydrocarbons, the accurate determination of the activation energies of the various modes of decomposition of the paraffins, the photodecomposition of the simple hydrocarbons, etc. The subject is, however, an exceedingly active one, and there is no reason to doubt that its rapid advance will be continued.

VI. REFERENCES

(1) ALLEN AND SICKMAN: J. Am. Chem Soc **56**, 2031 (1934).
(2) AMDUR AND ROBINSON: J. Am. Chem. Soc. **55**, 1395 (1933).
(3) BAIRSTOW AND HINSHELWOOD: J. Chem. Soc **1933**, 1155.
(4) BATES AND TAYLOR: J. Am. Chem Soc. **49**, 2438 (1927).
(5) BATES AND TAYLOR: J. Am. Chem. Soc. **50**, 771 (1928).
(6) BAWN: Trans. Faraday Soc. **32**, 178 (1936).
(7) BELCHETZ AND RIDEAL: Trans Faraday Soc. **30**, 170 (1934).
(8) BELCHETZ AND RIDEAL: J. Am. Chem. Soc. **57**, 1168 (1935).
(9) BELCHETZ AND RIDEAL: J Am. Chem. Soc. **57**, 2466 (1935).
(10) BERTHELOT: Compt. rend. **140**, 910 (1905).
(11) BERTHELOT: Notice sur les travaux scientifiques de M. Daniel Berthelot, Paris, 1917, p. 130. Quoted from Lind and Livingston (112).
(12) BERTHELOT AND GAUDECHON: Compt. rend. **150**, 1169 (1910).
(13) BEUTLER AND RABINOWITSCH: Z. physik. Chem. **B8**, 403 (1930).
(14) BODENSTEIN: Sitzungsber. preuss. Akad. Wiss **3**, 73 (1931).
(15) BODENSTEIN: Z. physik. Chem. **B12**, 151 (1931).
(16) BONE AND COWARD: J. Chem. Soc. **93**, 1197 (1908).
(17) BONE AND COWARD: Proc. Chem. Soc. (London) **24**, 167 (1908).
(18) BONE AND JERDAN: J. Chem. Soc. **71**, 41 (1897).
(19) BONE AND JERDAN: Proc. Chem. Soc. (London) **17**, 164 (1901).
(20) BONHOEFFER: Z. physik Chem. **113**, 199 (1924); **116**, 391 (1925).
(21) BONHOEFFER: Ergeb. exakt. Naturw. **6**, 201 (1927).
(22) BONHOEFFER: Z. Elektrochem. **40**, 425 (1934).
(23) BONHOEFFER AND HARTECK: Z. physik. Chem. **139**, 64 (1928).
(24) BURK: J. Phys. Chem. **35**, 2446 (1931)
(25) BURK, BALDWIN, AND WHITACRE: Ind. Eng. Chem. **29**, 326 (1937).
(26) CAMBRON: Can. J. Research **7**, 646 (1932).
(27) CANTELO: J. Phys. Chem. **30**, 899 (1926).
(28) CARIO AND FRANCK: Z. Physik **11**, 101 (1922).

(29) CHADWELL AND TITANI: J. Am. Chem. Soc. **55**, 1363 (1933).
(29a) DAVIS, JAHN, AND BURTON: J. Am. Chem. Soc. **60**, 10 (1938).
(30) DINZES AND FROST: J. Gen. Chem. (U. S. S. R.) **3**, 747 (1933).
(31) DINZES AND FROST: Compt. rend. acad. sci. U. R. S. S. **4**, 153 (1933).
(32) DINZES AND FROST: Compt. rend. acad. sci. U. R. S. S. **5**, 513 (1934).
(33) DINZES AND FROST: J. Gen. Chem. (U. S. S. R.) **4**, 610 (1934).
(33a) DINZES AND KLABINA: J. Gen. Chem. (U. S. S. R.) **7**, 1507 (1937).
(33b) DINZES, KVYATKOVSKII, STEPUKHOVICH, AND FROST: J. Gen. Chem. (U. S. S. R.) **7**, 1754 (1937).
(33c) DINZES, ZHARKOVA, ZHERKO, AND FROST: J. Gen. Chem. (U. S. S. R.) **7**, 1063 (1937).
(34) DINZES AND ZHERKO: J. Gen. Chem. (U. S. S. R.) **6**, 68 (1936).
(34a) DOBRONRAVOV AND FROST: J. Gen. Chem. (U. S. S. R.) **6**, 1796 (1936).
(35) DUNSTAN: Trans. Faraday Soc. **32**, 227 (1936).
(36) DUNSTAN, HAGUE, AND WHEELER: Ind. Eng. Chem. **26**, 307 (1934).
(37) EBREY AND ENGELDER: Ind. Eng. Chem. **23**, 1033 (1931).
(38) ECHOLS AND PEASE: J. Am. Chem. Soc. **58**, 1317 (1936).
(39) ECHOLS AND PEASE: J. Am. Chem. Soc. **59**, 766 (1937).
(40) EGLOFF: Reactions of the Pure Hydrocarbons. Reinhold Publishing Co., New York (1937).
(41) EGLOFF, BOLLMAN, AND LEVINSON: J. Phys. Chem. **35**, 3489 (1931).
(42) EGLOFF, LOWRY, AND SCHAAD: J. Phys. Chem. **36**, 1457 (1932).
(43) EGLOFF AND PARRISH: Chem. Rev. **19**, 145 (1936).
(44) EGLOFF AND SCHAAD: Chem. Rev. **6**, 91 (1929).
(45) EGLOFF, SCHAAD, AND LOWRY: J. Phys. Chem. **34**, 1617 (1930).
(46) EGLOFF, SCHAAD, AND LOWRY: J. Phys. Chem. **35**, 1825 (1931).
(47) EGLOFF, SCHAAD, AND LOWRY: Chem. Rev. **8**, 1 (1931).
(48) EGLOFF AND WILSON: Ind. Eng. Chem. **27**, 917 (1935).
(49) FARKAS: Ortho and Para Hydrogen and Heavy Hydrogen. Cambridge University Press, London (1935).
(50) FARKAS: J. Chem. Soc. **1936**, 26
(51) FARKAS AND MELVILLE: Proc. Roy. Soc. (London) **A157**, 625 (1936)
(52) FARKAS AND SACHSSE: Z. physik. Chem. **B27**, 111 (1935).
(53) FISCHER AND PICHLER: Brennstoff-Chem. **13**, 381 (1932).
(54) FISCHER AND PICHLER: Brennstoff-Chem. **13**, 406 (1932).
(55) FLETCHER AND ROLLEFSON: J. Am. Chem. Soc. **58**, 2129, 2135 (1936).
(56) FRANKENBURGER AND ZELL: Z. physik. Chem. **B2**, 395 (1929).
(57) FREY: Ind. Eng. Chem. **26**, 198 (1934).
(58) FREY AND HEPP: Ind. Eng. Chem. **25**, 441 (1933).
(58a) FREY AND HEPP: Ind. Eng. Chem. **28**, 1439 (1936).
(58b) FREY AND HUPPKE: Ind. Eng. Chem. **25**, 54 (1933).
(59) FREY AND SMITH: Ind. Eng. Chem. **20**, 948 (1928).
(60) FROST: J. Phys. Chem. (U. S. S. R.) **8**, 290 (1936).
(61) GEIB: Ergeb. exakt. Naturw. **15**, 68 (1936).
(62) GEIB AND HARTECK: Ber. **66**, 1815 (1932).
(63) GEIB AND HARTECK: Z. physik Chem. **A170**, 1 (1934).
(64) GEIB AND STEACIE: Z. physik. Chem. **B29**, 215 (1935).
(65) GEIB AND STEACIE: Trans. Roy. Soc. Can. III, **29**, 91 (1935).
(66) GROTH AND LAUDENKLOS: Naturwissenschaften **24**, 796 (1936).
(67) HAGUE AND WHEELER: J. Chem. Soc. **1929**, 378.

(68) Hague and Wheeler: Fuel **8**, 560 (1929).

(69) Heckert and Mack: J. Am. Chem. Soc. **51**, 2706 (1929).

(70) Heinemann: U. S. patent 1,134,677 (1915), 1,202,385 (1916).

(70a) Herzberg, Herzfeld, and Teller: J. Phys. Chem. **41**, 325 (1937).

(71) Hilgendorff: Z. Physik **95**, 781 (1935).

(72) Hinshelwood: Proc Roy. Soc (London) **A113**, 230 (1927).

(73) Hinshelwood and Hutchison: Proc. Roy. Soc. (London) **A111**, 380 (1926).

(74) Hirst: Proc Cambridge Phil. Soc. **23**, 162 (1926).

(75) Holliday and Exell: J Chem. Soc. **1929**, 1066.

(76) Holliday and Gooderham: J. Chem. Soc. **1931**, 1594.

(77) Hurd: Pyrolysis of Carbon Compounds. The Chemical Catalog Co., Inc., New York (1929).

(78) Hurd: Ind. Eng. Chem. **26**, 50 (1934).

(79) Hurd and Spence: J. Am. Chem. Soc. **51**, 3353 (1929).

(80) Jungers and Taylor: J. Phys. Chem. **3**, 338 (1935).

(81) Jungers and Taylor: J. Chem. Phys. **4**, 94 (1936).

(82) Kassel: J. Phys. Chem. **32**, 225 (1928).

(83) Kassel: J. Phys. Chem. **32**, 1065 (1928).

(84) Kassel: Kinetics of Homogeneous Gas Reactions. The Chemical Catalog Co , Inc., New York (1932).

(85) Kassel: Chem. Rev. **10**, 11 (1932).

(86) Kassel: J. Am. Chem. Soc. **54**, 3949 (1932).

(87) Kassel: J. Chem. Phys. **1**, 749 (1933).

(88) Kassel: J. Am. Chem. Soc. **57**, 833 (1935).

(89) Kato: Bull. Inst. Phys. Chem. Research (Tokyo) **10**, 343 (1931)

(90) Kemula: Roczniki Chem **10**, 273 (1930).

(91) Kemula: Collection Czechoslov. Chem. Commun. **7**, 319 (1935)

(92) Kemula: Collection Czechoslov. Chem. Commun. **7**, 493 (1935).

(93) Kemula and Mrazek: Z. physik. Chem. **B23**, 358 (1933).

(94) Kemula, Mrazek, and Tolloczko: Collection Czechoslov. Chem. Commun. **5**, 263 (1933).

(95) Kistiakowsky and Smith: J. Am. Chem. Soc. **58**, 766 (1936).

(95a) Kistiakowsky, Romeyn, Ruhoff, Smith, and Vaughan: J. Am. Chem. Soc. **57**, 65 (1935).

(96) Klemenc and Patat: Z. physik. Chem. **B3**, 289 (1929).

(97) Klemenc and Patat: Z. physik. Chem **A149**, 449 (1930).

(98) Krauze, Nemtzov, and Soskina: Compt. rend. acad. sci. U. R. S. S. **2**, 301 (1934).

(99) Krauze, Nemtzov, and Soskina: Compt. rend. acad꙼ sci. U. R. S. S. **3**, 262 (1934).

(100) Krauze, Nemtzov, and Soskina: J. Gen. Chem. (U. S. S. R.) **5**, 343 (1935).

(101) Krauze, Nemtzov, and Soskina: J. Gen. Chem. (U. S. S. R.) **5**, 356 (1935).

(102) Krauze, Nemtzov, and Soskina: J. Gen. Chem. (U. S. S. R.) **5**, 382 (1935).

(103) Landau: Compt. rend. **155**, 402 (1912).

(104) Leermakers: J. Am. Chem. Soc. **55**, 4508 (1933).

(105) Leermakers: J. Am. Chem. Soc. **56**, 1899 (1934).

(106) Leifson: Astrophys. J. **63**, 73 (1926).

(107) Leighton and Steiner: J. Am. Chem. Soc. **58**, 1823 (1936).

(108) Lenher: J. Am. Chem. Soc. **53**, 3752 (1931).

(109) Lind and Bardwell: J. Am. Chem. Soc. **48**, 1556 (1926).

(110) LIND AND LIVINGSTON: J. Am. Chem. Soc. **52**, 4613 (1930).
(111) LIND AND LIVINGSTON: J. Am. Chem. Soc. **54**, 94 (1932).
(112) LIND AND LIVINGSTON: J. Am. Chem. Soc. **55**, 1036 (1933).
(113) LIND AND LIVINGSTON: J. Am. Chem. Soc. **56**, 1550 (1934).
(114) LIND, JUNGERS, AND SCHIFLETT: Phys. Rev. **46**, 825 (1934).
(115) LIVINGSTON AND SCHIFLETT: J. Phys. Chem. **38**, 377 (1934).
(116) McDONALD AND NORRISH: Proc. Roy. Soc. (London) **A157**, 480 (1936)
(117) MAREK AND HAHN: Catalytic Oxidation of Organic Compounds in the Vapor Phase. The Chemical Catalog Co., Inc., New York (1932).
(118) MAREK AND McCLUER: Ind. Eng. Chem. **23**, 878 (1931).
(119) MAREK AND NEUHAUS: Ind. Eng Chem. **24**, 400 (1932).
(120) MAREK AND NEUHAUS: Ind. Eng. Chem. **25**, 516 (1933).
(121) MECKE: Z. physik. Chem. **B7**, 108 (1930).
(122) MECKE: Z. Elektrochem. **36**, 595 (1930).
(123) MECKE: Trans. Faraday Soc. **27**, 374 (1931).
(124) MELVILLE: J. Chem. Soc. **1934**, 1243.
(125) MELVILLE: Trans. Faraday Soc. **32**, 258 (1936).
(126) MITCHELL AND HINSHELWOOD: Proc. Roy. Soc. (London) **A159**, 32 (1937).
(126a) MITSENGENDLER: J. Gen. Chem. (U. S S. R.) **7**, 1848 (1937).
(127) MOONEY AND LUDLAM: Trans Faraday Soc. **25**, 442 (1929).
(127a) MOOR, FROST, AND SHILYAEVA: J. Gen. Chem. (U S. S R.) **7**, 818 (1937).
(127b) MOOR, STRIGALEVA AND FROST: J. Gen. Chem. (U S. S R) **7**, 860 (1937).
(128) MOOR, STRIGALEVA, AND SHILYAEVA: J. Gen. Chem. (U. S S S. R.) **5**, 818 (1935).
(129) MORIKAWA, BENEDICT, AND TAYLOR: J. Chem. Phys. **5**, 212 (1937).
(130) MUND AND JUNGERS: Bull. soc. chim. Belg **40**, 158 (1931).
(131) MUND AND KOCH: Bull. soc. chim. Belg. **34**, 125, 241 (1925)
(132) NORRISH: Proc. Roy. Soc. (London) **A150**, 36 (1935)
(132a) NORRISH, CRONE, AND SALTMARSH: J. Chem. Soc. **1934**, 1456.
(133) OLSON AND MEYERS: J. Am. Chem. Soc. **48**, 389 (1926).
(133a) OLSON AND MEYERS: J. Am. Chem. Soc. **49**, 3131 (1927).
(134) PANETH AND HOFEDITZ: Ber. **62**, 1335 (1929).
(134a) PANETH, HOFEDITZ, AND WUNSCH: J. Chem. Soc. **1935**, 372.
(134b) PARKS: Chem. Rev. **18**, 325 (1936).
(135) PATAT: Z. physik. Chem. **B32**, 274 (1936).
(136) PATAT: Z. physik. Chem. **B32**, 294 (1936).
(137) PATAT AND SACHSSE: Z. Elektrochem. **41**, 493 (1935)
(138) PATAT AND SACHSSE: Nachr. Ges. Wiss. Göttingen III, **1**, 41 (1935)
(139) PAUL AND MAREK: Ind. Eng. Chem. **26**, 454 (1934).
(140) PEASE: J. Am. Chem. Soc. **50**, 1779 (1928).
(141) PEASE: J. Am. Chem. Soc. **51**, 3470 (1929).
(142) PEASE: J. Am. Chem. Soc. **52**, 1158 (1930).
(143) PEASE: J. Am. Chem Soc. **53**, 613 (1931).
(144) PEASE: J. Am. Chem Soc. **54**, 1876 (1932).
(145) PEASE AND CHEESEBRO: Proc. Natl. Acad. Sci. U. S. **14**, 472 (1928).
(146) PEASE AND DURGAN: J. Am. Chem Soc. **50**, 2715 (1928).
(147) PEASE AND DURGAN: J. Am. Chem. Soc. **52**, 1262 (1930).
(148) PEASE AND MORTON: J. Am. Chem. Soc. **55**, 3190 (1933).
(149) PEASE AND WHEELER: J. Am Chem. Soc. **57**, 1144 (1935).
(150) PETERS AND WAGNER: Z. physik. Chem. **A153**, 161 (1931).
(151) PRICE: Phys. Rev. **45**, 843 (1934).

(152) PRICE: Phys Rev. **47**, 444 (1935).
(153) PRING AND FAIRLIE: J Chem Soc **99**, 1796 (1911).
(154) PRING AND HUTTON: J. Chem. Soc. **89**, 1591 (1906).
(155) REINICKE: Z angew Chem. **41**, 1144 (1928).
(156) RICE, F. O : J Am. Chem. Soc. **53**, 1959 (1931).
(157) RICE, F. O : J Am. Chem. Soc. **55**, 3035 (1933).
(158) RICE, F. O.: J Am Chem. Soc. **56**, 488 (1934).
(159) RICE, F O.: Trans Faraday Soc. **30**, 152 (1934).
(160) RICE, F. O , AND DOOLEY: J. Am. Chem. Soc. **55**, 4245 (1933).
(161) RICE, F. O , AND DOOLEY: J Am. Chem Soc. **56**, 2747 (1934).
(162) RICE, F. O., AND HERZFELD: J. Am Chem. Soc. **56**, 284 (1934).
(163) RICE, F O , AND JOHNSTON: J. Am Chem. Soc. **56**, 214 (1934).
(164) RICE, F. O., JOHNSTON, AND EVERING: J. Am Chem. Soc. **54**, 3529 (1932).
(165) RICE, F. O., AND POLLY: Ind Eng. Chem. **27**, 915 (1935).
(166) RICE, F. O , AND RICE, K. K : The Aliphatic Free Radicals. Johns Hopkins Press, Baltimore (1935).
(167) RICE, O K : Proc Natl. Acad. Sci. U. S. **14**, 113 (1928).
(168) RICE, O K , AND RAMSPERGER: J. Am. Chem. Soc. **49**, 1617 (1927).
(169) RICE, O. K., AND RAMSPERGER: J. Am. Chem. Soc. **50**, 617 (1928).
(170) RICE, O K , AND SICKMAN: J. Am. Chem Soc. **57**, 1384 (1935)
(171) RIDEAL: Proc Roy. Soc. (London) **A146**, 266 (1934).
(172a) RIEKE: J. Chem Phys **4**, 513 (1936).
(172a) ROSSINI: Ind. Eng Chem. **29**, 1424 (1937).
(172b) ROSSINI AND KNOWLTON: J. Research Natl. Bur. Standards **19**, 339 (1937).
(173) RUDDER AND BIEDERMANN: Bull. soc. chim. **47**, 710 (1930).
(174) SACHSSE: Z physik Chem. **B31**, 87 (1935).
(175) SACHSSE: Z. physik. Chem. **B31**, 79 (1935).
(176) SACHSSE: J. Chem. Phys **5**, 199 (1937).
(177) SCHEIBE AND LINDSTRÖM: Z. physik. Chem. **B12**, 387 (1931).
(178) SCHEIBE, POVENZ, AND LINDSTRÖM: Z. physik. Chem. **B20**, 283 (1933).
(179) SCHEIBE AND GRIENEISEN: Z. physik. Chem. **B25**, 52 (1934).
(180) SCHLÄPFER AND BRUNNER: Helv. Chim. Acta **13**, 1125 (1930).
(181) SCHMIDT: Z Elektrochem. **39**, 969 (1933).
(182) SCHNEIDER AND FROLICH: Ind. Eng. Chem. **23**, 1405 (1931).
(183) SEMENOFF: Chemical Kinetics and Chain Reactions. Cambridge University Press, London (1935).
(183a) SEREBRYAKOVA AND FROST: J. Gen. Chem. (U. S. S. R.) **7**, 122 (1937).
(184) SICKMAN AND ALLEN: J. Am. Chem. Soc. **56**, 1251 (1934).
(185) SICKMAN AND RICE, O. K.: J. Chem. Phys. **4**, 608 (1936).
(186) SMALLWOOD: J. Am. Chem. Soc. **56**, 1542 (1934).
(187) SMITH, GRANDONE, AND RALL: U. S. Bur. Mines Rept. Investigations **3143**, (1931).
(187a) SMITH AND VAUGHAN: J. Chem. Phys. **3**, 341 (1935).
(188) STANLEY AND NASH: J. Soc. Chem. Ind. **48**, 1T, (1929).
(188a) STAVELEY: Proc. Roy. Soc. (London) **A162**, 557 (1937).
(188b) STAVELEY AND HINSHELWOOD: Proc. Roy. Soc. (London) **A154**, 335 (1936).
(189) STAVELEY AND HINSHELWOOD: Nature **137**, 29 (1936).
(190) STAVELEY AND HINSHELWOOD: J. Chem. Soc. **1936**, 812.
(191) STAVELEY AND HINSHELWOOD: Proc. Roy. Soc. (London) **A159**, 192 (1937).

(191a) STAVELEY AND HINSHELWOOD: J. Chem. Soc. **1937**, 1568.
(192) STEACIE: Can. J. Research **15B**, 264 (1937).
(192a) STEACIE: J. Chem. Phys. **6**, 37 (1938).
(193) STEACIE AND ALEXANDER: J. Chem. Phys. **5**, 372 (1937); Can. J. Research, **B15**, 295 (1937).
(194) STEACIE AND FOLKINS: Unpublished work.
(195) STEACIE AND KATZ: J. Chem. Phys. **5**, 125 (1937).
(196) STEACIE AND PHILLIPS: J. Chem. Phys. **4**, 461 (1936).
(197) STEACIE AND PHILLIPS: J. Chem. Phys. **5**, 275 (1937).
(198) STEACIE AND PHILLIPS: J. Chem. Phys., in press.
(198a) STEACIE AND PUDDINGTON: Unpublished work.
(199) STORCH: J. Am. Chem. Soc. **54**, 4185 (1932)
(200) STORCH: Ind. Eng Chem. **26**, 56 (1934).
(201) STORCH: J. Am. Chem. Soc. **56**, 374 (1934).
(202) STORCH: J. Am. Chem. Soc. **57**, 2598 (1935).
(203) STORCH AND GOLDEN: Ind. Eng. Chem. **25**, 768 (1933)
(203a) STORCH AND KASSEL: J. Am. Chem. Soc. **59**, 1240 (1937).
(204) STUART: Molekülstruktur. Springer, Berlin (1934).
(205) TAYLOR, H. A., AND VAN HOOK: J. Phys. Chem **39**, 811 (1935).
(206) TAYLOR, H. S : Trans. Faraday Soc. **21**, 560 (1925).
(207) TAYLOR, H. S.: Proc. Am. Phil. Soc. **65**, 90 (1926).
(208) TAYLOR, H. S.: Ind. Eng. Chem. **20**, 439 (1928).
(209) TAYLOR, H. S., AND BATES: Proc. Natl Acad. Sci. U. S. **12**, 714 (1926).
(210) TAYLOR, H. S., AND EMELEUS: J. Am. Chem. Soc. **52**, 2150 (1930).
(211) TAYLOR, H. S., AND EMELEUS: J. Am. Chem. Soc. **53**, 562 (1931).
(212) TAYLOR, H. S., AND EMELEUS: J. Am. Chem. Soc. **53**, 3370 (1931).
(213) TAYLOR, H. S., AND HILL: Z. physik. Chem. **B2**, 449 (1929).
(214) TAYLOR, H. S., AND HILL: J. Am. Chem. Soc. **51**, 2922 (1929).
(215) TAYLOR, H. S., AND JONES: J. Am. Chem. Soc. **52**, 1111 (1930).
(215a) TAYLOR, H. S., AND JUNGERS: Trans. Faraday Soc. **33**, 1353 (1937).
(216) TAYLOR, H. S , AND MARSHALL: J. Phys. Chem. **29**, 1140 (1925).
(217) TAYLOR, H. S., MORIKAWA, AND BENEDICT: J. Am. Chem. Soc. **57**, 383 (1935).
(218) THENARD: Compt. rend. **78**, 219 (1874).
(218a) THOMAS, EGLOFF, AND MORRELL: Ind. Eng. Chem **29**, 1260 (1937).
(219) TOLLOCZKO: Przemysl Chem. **11**, 245 (1927).
(220) TOUL: Collection Czechoslov. Chem. Commun. **6**, 163 (1934).
(221) TOUL: Collection Czechoslov. Chem. Commun. **7**, 491 (1935).
(222) TRAVERS: Nature **138**, 967 (1936).
(222a) TRAVERS: J. Indian Chem. Soc., P. C. Ray Commemorative Vol., p. 17 (1933).
(222b) TRAVERS: Trans. Faraday Soc. **33**, 1342 (1937).
(222c) TRAVERS: Trans. Faraday Soc. **33**, 751 (1937).
(223) TRAVERS AND HOCKIN: Proc. Roy. Soc. (London) **A136**, 1 (1932)
(224) TRAVERS AND HOCKIN: Trans. Faraday Soc. **32**, 236 (1936).
(225) TRAVERS AND PEARCE: J. Soc. Chem. Ind. **53**, 321T (1934).
(226) TRENNER, MORIKAWA, AND TAYLOR, H. S.: J. Chem. Phys. **5**, 203 (1937).
(227) TROPSCH AND EGLOFF: Ind. Eng. Chem. **27**, 1063 (1935).
(228) VAUGHAN: J. Am. Chem. Soc. **54**, 3863 (1932).
(229) VAUGHAN: J. Am. Chem. Soc. **55**, 4109 (1933).
(229a) VOGE: J. Chem. Phys. **4**, 581 (1936).

(230) von Hartel and Polanyi: Z. physik. Chem. **B11,** 97 (1930).

(231) von Wartenberg and Schultze: Z. physik. Chem. **B2,** 1 (1929).

(231a) Vvedenskii, Vinnikova, and Frost: J. Gen. Chem. (U S. S. R.) **4,** 120 (1934).

(232) Wheeler and Pease: J. Am. Chem. Soc. **58,** 1665 (1936).

(233) Wheeler and Wood: J. Chem. Soc. **1930,** 1819.

(234) Wheeler and Wood: Fuel **9,** 567 (1930).

(235) Witham: Ph.D. Thesis, Columbia University, 1934 (quoted from Egloff (40)).

(236) Wood: Proc. Roy. Soc. (London) **A104,** 1 (1923).

(237) Zelinsky: Ber. **57,** 264 (1924).

THEORIES FOR THE MECHANISM OF THE SETTING OF SILICIC ACID GELS

CHARLES B. HURD

Department of Chemistry, Union College, Schenectady, New York

I. INTRODUCTION

Any theory which will successfully explain the mechanism involved in the setting of gels of hydrated silica, or silicic acid gels, as they are commonly called, should explain not only the properties of the gel when set but also any of the phenomena observed during the setting process. The present paper presents not only a discussion of the various theories which have been proposed, but also such observations of various investigators in the field of silicic acid gels as may appear important in the discussion.

In order that this paper may be kept within reasonable limits, no attempt is made to present a complete bibliography, nor can more than one vital reference be cited, ordinarily, for each point. More extensive bibliographies are available in the literature (79, 6).

The matter of terminology should be clarified at the start. By the term "colloidal silicic acid," or "sol of hydrated silica," will be understood the fluid mixture containing hydrated silica. The term "silicic acid gel," or "gel of hydrated silica," will indicate the semisolid elastic mass which results when the gel has, as we say, set. The term "silica gel" will be used to designate the harder, partially dehydrated product.

The presentation of the theories for the setting of the gel will be made easier if we first consider the various methods of preparation of sol and gel, the significant phenomena during the sol-to-gel transformation known as setting and, lastly, any properties of the sol and gel which substantiate or refute the various theories.

II. PREPARATION OF SOLS OF HYDRATED SILICA

Colloidal silicic acid has been known for about two hundred years. Berzelius (4) mentioned that he prepared "soluble" silicic acid by the action of ammonium hydroxide upon hydrofluorosilicic acid. What he had prepared was a sol of hydrated silica. A reference to earlier work is given by Walden (76).

Probably the most common method consists of the action of a solution

of sodium silicate and an acid, as performed by Graham (24) and many others. Some investigators have used a solution of an ammonium salt instead of the acid (5).

By electrolysis of solutions of sodium silicate, Treadwell and Wieland (74) and Kröger (48) have removed nearly all of the sodium by deposition in a special mercury cathode. A reference will be made later to the fact that they reduced the hydroxyl-ion concentration as well as the sodium-ion concentration. They prepared relatively stable sols. Their process consisted practically of the hydrolysis of the sodium silicate solution and the nearly complete removal of the sodium hydroxide.

The hydrolysis of various silicon compounds has been used to prepare sols of hydrated silica, among them the chloride (51), the fluoride (14), the sulfide (19), and a number of esters of orthosilicic acid (13), such as methyl silicate (25).

Mention of these methods may introduce an objection—namely, that with the silicic acid other substances are formed in the solution. Many investigators have removed the greater portion of these soluble impurities by dialysis, but at least the colloidal silicic acid was first formed in their presence. Also, dialysis apparently never removes the last traces of electrolytes.

Two methods have apparently avoided the presence of these impurities in the original sol. The first of these was the preparation of colloidal silica by Lenher (54), who ground Ottawa sand to a fine powder and then heated it to 300–400°C. with water in a bomb. He was able to hydrate the silica. The other is the method of Kargin and Rabinovich (42), who oxidized silane (SiH_4) by means of ozonized oxygen in the presence of water.

Sols have been prepared by peptizing freshly prepared silicic acid gel by means of ammonium hydroxide (69) or potassium hydroxide (45). The peptizing agent was then removed.

III. PREPARATION OF SILICIC ACID GEL

Silicic acid gels result from practically any sol of hydrated silica, merely with the lapse of time. It is essential, of course, that the sol contain a large enough concentration of silica to give sufficient strength or rigidity for the gel to set. A sol which contains less than 0.5 per cent SiO_2 will give a very weak gel, or no gel at all. Sols which are strongly alkaline may not set at all.

Certain conditions, such as concentration of silica, temperature, hydrogen-ion concentration, and concentration of other substances, will be found to govern the time required for gelation or "time of set", as it is called, but it is safe to say that any sol containing over 2 per cent SiO_2 will set eventually to a gel, unless it is strongly alkaline.

Methods, therefore, for the preparation of silicic acid gel are essentially those for the preparation of the hydrosol of silica. Some time may be required for the gel to set.

IV. THE SOL–GEL TRANSFORMATION OR SETTING OF THE GEL

The sol of hydrated silica, when first prepared, is transparent. The viscosity is practically that of water. As the material stands, a faint opalescence becomes apparent which increases, ordinarily, until after the gel has set. The viscosity shows no noticeable change until the opalescence becomes quite marked. Then the viscosity increases rapidly, and soon the material develops elasticity, showing not only the resistance to flow characteristic of the increasing viscosity, but also a rapidly increasing tendency for the material to resist a stress and to return toward its original form after deformation. Any of the various tests will soon show that the gel has set. The setting process continues, of course, for some time after the test pronounces the gel set. Probably this fact is most clearly shown by the optical method of Prasad, Mehta, and Desai (66).

V. SIGNIFICANT PROPERTIES OF THE SOL OF HYDRATED SILICA

When first formed, the silicic acid appears to be in the form of simple molecules of low molecular weight. This has been shown by many investigators. Gruner and Elöd (27) found an apparent molecular weight of 60 in a freshly prepared sol, as did Willstätter, Kraut, and Lobinger (80). Treadwell (72) reported the first value to be 149. The apparent molecular weight has been found to increase rapidly with time, however, showing in the work of H. and W. Brintzinger (8) a value of 8260 after 45 days. Since, in all of these molecular weight determinations, an allowance has been made for electrolytes present in the solution, one can not feel too certain of the absolute value of the molecular weight of the silicic acid. The first low values are, however, undoubtedly reliable, and the trend toward the higher values is certainly indicated.

When first formed, considerable silicic acid passes easily with the electrolytes through the membranes used for dialysis. With the lapse of time, all of the silicic acid becomes unable to pass through the membrane. This fact, as well as the change in molecular weight, points unmistakably to the belief that silicic acid, when first formed, consists of small molecules, but that with the lapse of time these condense, polymerize, or coalesce to form large groups.

Mylius and Groschuff (59) have used albumin to test the silicic acid formed. At first they found that it would not coagulate albumin, a characteristic which they ascribe to simple molecules. They call this

form α-silicic acid.   Upon standing, α-silicic acid goes over into the β-form, the molecules of which, being larger, do coagulate albumin.

Although Karsten (43) claimed that hydrochloric acid forms a partial or temporary compound with silicic acid, this point of view appears completely disproven.   Although it does appear impossible to remove the last traces of impurities, especially electrolytes, by dialysis, it has also been shown that silver nitrate will react with the chloride ion in the sols containing this minimum of chloride ion.   In this respect these silicic acid sols would, therefore, show a marked difference from alumina sols containing a little chloride, as explained by Thomas (71).

Probably this difficulty of removing residual traces of electrolytes from these sols of hydrated silica serves to explain the divergence in pH values measured.   A pH as low as 3.2 was reported by Rabinovich and Laskin (67), while Brintzinger and Troemer (9) found a value of 4.6.   Upon washing gelatinous silicic acid by means of a supercentrifuge, Bradfield (7) found that the pH approached 6.5, whether he started with alkaline or acid mixtures.   The sol prepared by Kargin and Rabinovich (42) by the oxidation of silane gave a pH very nearly 7.0.

An unfortunate feature of these measurements is that they give the pH for a sol, not just as it is formed, but after it has stood for some time, during which time the process of condensation has undoubtedly progressed for some distance.   They fail, therefore, to inform us concerning the silicic acid when first formed.

The electrical charge on the particles of the sol has been shown by Losenbeck (55) to be negative in alkaline, neutral, or weakly acid solution.   In more strongly acid solution the particles become positively charged.   The idea has been held that this charge is entirely due to preferential adsorption, but it will be shown in this paper that it is probably due to the ionization of the silicic acid, which, owing to the amphoteric character of the molecule, occurs in two ways, leaving the silicon in either a negative or positive ion.

One of the most striking properties of the particles in a sol of hydrated silica is their great insensitivity toward ions which ordinarily cause coagulation of colloids.   This has been shown by Laskin (52) and others.   The data available, while confusing, in general, demonstrate conclusively this insensitivity of the colloidal silicic acid toward electrolytes.

The sols at first show no Tyndall cone, but this develops as they stand (47).   They probably show no optical rotation (12), although the data are not absolutely conclusive.   Microscopic studies have failed to detect any visible structures in the sol, or even in the gel, for that matter.   The ultramicroscopic data are not at all conclusive.

The statement has been made that the silicic acid present in a sol con-

taining hydrochloric acid has a small effect in decreasing the conductivity of the hydrochloric acid (55).   The conductivity of sols of hydrated silica has been found to change very little, if at all, even when the mixture sets to form a gel (59, 23).

VI. FACTORS GOVERNING THE TIME OF SET

Among the factors which affect the time of set of silicic acid gels are the concentration of silica, the temperature, the acid used, the hydrogen-ion concentration, and the concentrations of other materials present.

It is a well-known fact that the higher the silica concentration the more rapidly will the gel set.   Some study has been made of this factor, but a thorough investigation is needed.

The fact that a rise of temperature hastened the setting of silicic acid was noted by Maschke (56) and many others.   Although the earlier work (15) failed to find any definite relation between temperature and time of set, recent work by Hurd and Miller (38) has demonstrated that the effect of temperature upon the time of set of gels produced by mixing solutions of sodium silicate and acetic acid is the same, regardless of the soda–silica ratio of the sodium silicate used.   By considering the process as a chemical reaction, they obtained a value for the energy of activation for the process of 16,640 calories.   As a result of further studies, Hurd (32) has shown that the energy of activation is practically the same using either acetic, citric, succinic, or tartaric acid, all, of course, being weak acids.

The use of strong acids adds the complication of a change in pH of the mixture during setting.   By making allowances for this (34) it is possible to show that the energy of activation is approximately the same when strong acids are used.

The earlier investigators observed that, in acid gel mixtures, an increase in the concentration of acid also increased the time of set greatly (56). The curve for time of set against concentration of hydrochloric acid was plotted by Holmes (29), and was found to give a peculiar hump.   This showed a minimum time of set in faintly alkaline solutions, as was also observed earlier by Fleming (18), and later by Hurd and Letteron (37) and by Prasad and Hattiangadi (65).   Holmes also showed that at high concentrations of acid the time of set diminishes.   The optimum limits of pH consistent with setting have been reported by Ray and Ganguly (68).

In a quantitative study of the relation between hydrogen-ion concentration and time of set, Hurd, Raymond, and Miller (39) have shown that for acid gels prepared from sodium silicate and acetic or hydrochloric acid between pH $= 4.0$ and 6.0, the time of set shows a linear relation to the hydrogen-ion concentration.   In the same study, it was shown that if a constant hydrogen-ion concentration were maintained in mixtures con-

taining increasing concentrations of acetic acid by addition of the correct amount of sodium acetate, the time of set was very slightly affected by the concentration of acetic acid. This would indicate that the hydrogen-ion concentration, rather than the concentration of acid, is the important factor in governing the rate of the setting process.

Work in alkaline gel mixtures presents much greater difficulties, due chiefly to the variation of the hydrogen-ion concentration. We may state, however, from completed but unpublished work in this laboratory, that in alkaline gel mixtures an approximately linear relation exists between time of set and hydroxyl-ion concentration.

The data available upon the effect of various electrolytes and non-electrolytes upon the time of set of silicic acid gel mixtures show considerable lack of agreement. As Hurd and Carver (33) have pointed out, this has arisen in many instances because of neglect of the simultaneous change of the hydrogen-ion concentration. This was particularly true in the case of ammonia, the amines, and pyridine.

It is apparently true that some non-electrolytes show a specific effect upon the time of set of these silicic acid gel mixtures. The effect is usually greater in alkaline gel mixtures than in acidic mixtures, as shown by Munro and Alves (58). They showed, as did Hurd and Carver, that glycerol caused an increase in the time of set, a fact which is very surprising when one considers the dehydrating power of glycerol. The main point to be noted here appears to be that non-electrolytes have little effect unless added in reasonably large amounts (traces show no effect at all), and that they affect alkaline gel mixtures more than acid mixtures.

The effect of salts upon the time of set is also not particularly marked. For example (39), it was shown that a concentration of sodium chloride of $1\,M$ in a gel mixture produced from sodium silicate and acetic acid decreased the time of set by half. A similar concentration of sodium sulfate decreased the time of set by about 20 per cent.

The effect of radiant energy upon the time of set has not been fully studied. Although Ray and Ganguly have noted that ultraviolet light accelerated the setting, the effect of all forms of radiant energy must be small, if the thermal effects are excluded. One can easily show this by determining the very small difference between the times of set for two portions of the same mixture, one in the light and the other in the dark.

VII. PROPERTIES OF SILICIC ACID GELS

Certain specific properties of silicic acid gels interest us here because of their bearing upon the several theories for the mechanism of the setting process. These properties are the elasticity of the gel, syneresis, thixotropy, the apparently very high molecular weight, the failure to retain

chloride, the results of magnetic analysis, the x-ray analysis, and the electrical conductivity.

Attempts have been made for many years to obtain conclusive evidence of the presence of definite silicic acids or definite hydrates of silica in the sol of hydrated silica or, more particularly, in coagulated silicic acid or in the gel. To cite merely two references, the work of Tschermak (75) and others has been interpreted to show the existence of several definite silicic acids, among them ortho-, meta-, or pyro-silicic acid. Schwarz (70) has claimed that two different kinds of water are in the gel,—free water and bound water. The latter may be considered as chemically combined.

The opposite point of view—namely, that the gel does not contain definite hydrates—was stated by van Bemmelen (3), whose extended studies on the hydration and dehydration of silicic acid gel failed to show the existence of any definite hydrates. Pascal's (64) magnetic analysis showed no evidence of the existence of ortho-, meta-, or pyro-silicic acids, but did show that the material consisted of silica and water. The x-ray determinations by Krejci and Ott (46) showed the cristobalite pattern.

The sol of hydrated silica, as it is setting, suddenly shows the development of elasticity. No comprehensive data on this development are available, but, as Langmuir (50) has observed, the material shows a stretch up to a certain limit, somewhat like rubber bands. As the gel sets, the limits of this stretch become smaller. According to Holmes (30) this elasticity is due, in part, to the tension developed in the gel.

Syneresis appears to be due to a contraction of the gel after it has set, resulting in the expression of a certain amount of fluid. It has been studied especially by Gaunt and Usher (22). The condensation and shrinkage, apparently, occur for some time after the gel has set, the extent of syneresis depending upon various factors (30), among them the concentration of silica, the hydrogen-ion concentration, and the temperature.

The phenomenon of thixotropy is shown by the gel mixture in the early stages of setting, that is, the gel will knit itself together after being stirred or separated. This power is lost after the gel has set. The behavior of silicic acid gel in this respect differs somewhat from the ordinary gels which show thixotropy.

Silicic acid gel is affected very little if treated with strong acid. On the other hand, a solution of sodium hydroxide will dissolve the gel quickly and easily.

The fact that little, if any, change occurs in the electrical conductivity during the sol–gel transformation is of great importance.

There is practically no thermal effect when the gel sets (74). This has occasioned some comment in the literature, but it will be shown that the result is exactly as would be expected.

Theories of gel structure, although they show many different character-istics, fall naturally into three general classes. The large number of in-dividual modifications of the basic theories has resulted from the fact that many workers in the field have discovered and investigated an almost unlimited number of gels. The reader interested in the general subject of gels and gel structure is referred to the papers by Ostwald (61) and von Weimarn (78). The many gels investigated show differences in properties, not only differences of degree, but often of type.

The words "jelly" and "gel" have been used in a different sense by many writers, the usual custom being to use "jelly" for the more dilute, elastic type, such as a gelatin jelly, and to use the word "gel" for the partially dehydrated product known technically as silica gel. The writer will use the word "gel", particularly "silicic acid gel," throughout this paper.

The three general theories for gel structure are: (A) the emulsion theory; (B) the cellular theory; and (C) the fibrillar or micellar theory.

Specialists in colloid chemistry will note the omission of what is fre-quently called the solid solution theory (44). This really is not a theory of gel structure, but refers to a mechanism by which solvent is imbibed in the process known as swelling. While it postulates, for example, that water enters gelatin in the form of a solution in the solid, it does not explain the resulting structure.

An attempt will now be made to consider each of the three theories, in order to present a satisfactory theory for the structure of silicic acid gel. We shall consider those properties of the sol and gel of silicic acid which aid in confirming or disproving the theory.

A. The emulsion theory

This theory was explained by Ostwald (62, 61). The theory assumes that the gel consists of a liquid–liquid system with an emulsoid structure, although Ostwald pointed out that he considered both liquids to be ab-normal and one somewhat more concentrated than the other. The theory did not receive Ostwald's complete support in the case of silicic acid gel, but he did consider it as a possibility, perhaps explaining a temporary structure formed during the setting of silicic acid gel.

The theory fails, in the case of silicic acid gels, when one considers viscosity and elasticity. An emulsion is characterized by a high viscosity, but it does possess the ability to flow. Dilute silicic acid gels show con-siderable flow when subjected to a deforming force. As the concentration of silica increases, the gels show greater elasticity and less tendency to

flow. Gels containing over 3 per cent silica flow very little when subject to a force. This problem has not been thoroughly studied.

The calculations of Hatschek (28) of a series of stress–strain curves, assuming an emulsoid structure for gels, and the failure of these curves to agree in any particular with measured stress–strain curves for gelatin and rubber are often quoted as a general refutation of the emulsoid structure for gels. While the proper work has, apparently, not been done on the elasticity of freshly formed silicic acid gel, it does appear that the gel follows Hooke's law. It has a low elastic limit.

At present the weight of opinion is very decidedly against the emulsion theory for any gel.

B. The cellular theory

This theory, which is credited to Bütschli (11), postulates that the liquid part of the gel is held in the form of small droplets in a cellular structure made up of the solid phase. The theory is sometimes called the honeycomb theory, because of the assumed structure of the framework.

While a cellular framework has actually been observed microscopically in the case of some gels, such as von Weimarn's (77) barium sulfate gels, there is the best of evidence to show that Bütschli's observations showed something much coarser than the original structure. His estimates gave a wall thickness in silicic acid gel of 0.3μ, while the pockets appeared to be from 1.0 to 1.5μ in diameter. The work of Zsigmondy (81) gave an estimate of 5 mμ for the pore diameter for silicic acid gel, while Anderson's (1) estimate showed even smaller pores. Such a structure could not possibly be observed by the microscope, being several hundred times as small as the structures seen by Bütschli.

The gels in which von Weimarn observed the cellular structure were very different from silicic acid gels, and were called by him coarse-cellular gels. They were made by mixing two concentrated solutions of inorganic substances into a coarse mixture like an emulsion. The reaction precipitated material along the boundary surfaces.

The cellular structure best explains the retention of water in a gel such as silicic acid gel. While gels such as the barium malonate gel (17) have been discovered, from which some water may be withdrawn even by touching the gel with filter paper, the same thing is not true of silicic acid gel, which holds the water much more firmly. Yet, while the cellular structure explains well the ability of silicic acid gel to hold water, it does not provide any satisfactory explanation for syneresis, nor for the phenomena observed when water evaporates from a silicic acid gel.

Soon after a silicic acid gel has set, liquid appears upon its surface. This squeezing out of some of the fluid is called syneresis. It has been studied

by Gaunt and Usher (22), by Kuhn (49), and especially in silicic acid gels by Ferguson and Applebey (16). Syneresis appears to occur to a much smaller degree as the gel becomes older. The fluid is a solution of the salts or acids present. It is difficult to see how this fluid could be squeezed out by the gel without destroying its cellular structure.

When a cylinder of silicic acid gel is allowed to stand in the air it will shrink, retaining approximately its original proportions. If the structure were cellular, it seems reasonable to suppose that water would come most easily from the outer cells, and that distortion or cracking would result.

A serious point against the cellular theory for silicic acid gels is that practically no increase in the electrical resistance occurs when the gel mixture sets (40). This fact has been mentioned previously and is true in the case of gels other than silicic acid gels. It is difficult to conceive of the formation of solid or semisolid walls, cutting up the gel into small cells containing fluid, without a noticeable increase in electrical resistance.

A cellular structure would explain very satisfactorily the elasticity of silicic acid gels. This, and the explanation of a structure to hold the fluid portion of the gel, are the chief points in favor of the cellular theory.

C. The fibrillar theory

The fibrillar or micellar theory is sometimes called the sponge theory (79). It is usually credited to Nägeli (60). It postulates a solid and a liquid phase, each continuous, with the solid forming a fibrous structure and containing the liquid in the pores. It is the theory favored by most workers in the field. The differences in their points of view relate to the method of forming this fibrillar structure. They may be considered under three general headings.

(1) Structure formed by coagulation of the colloid. Many workers have believed that a silicic acid gel is formed simply by the coagulation of the silicic acid or hydrated silica in the sol. The structure of the gel would result from the mechanical agglomeration of the colloid, which would leave spaces filled with water. This was suggested by Pappada and Sadowsky (63).

This would be a very simple mechanism, if it were verified. Practically, however, the weight of evidence is against it. It is readily apparent that sols of hydrated silica are very insensitive to coagulation by electrolytes (52). The setting of a silicic acid gel resembles in no way the coagulation of a sol, such as arsenious sulfide sol. There the addition of low concentrations of the ion of correct charge, particularly a polyvalent ion, will cause a cloudy appearance within a few seconds, followed very shortly by a coagulation of the precipitate. Nothing resembling this behavior occurs with silicic acid. The sol is not coagulated by either positive or negative

ions in low concentrations, even by polyvalent ions. Nevertheless there are many contributions in the literature by those, such as Prasad and Hattiangadi (65), who believe that silicic acid gel results from coagulation of the sol by ions. Some writers even go so far as to discuss the effect of non-electrolytes upon the power of various ions for coagulating the sol of hydrated silica.

Without entering into a long discussion, the writer must rest the case with the following example, taken from the paper by Hurd, Raymond, and Miller (39). A sol of hydrated silica containing the following concentrations in gram-moles per liter—SiO_2, 0.645; Na^+, 0.385; CH_3COO^- and excess CH_3COOH, 0.502—and having a pH of 5.09 set in 53 minutes. The addition of 0.500 gram-mole of sodium sulfate per liter to the original mixture decreased the time of set to 44 minutes. The same concentration of sodium chloride in another mixture decreased the time of set to 28 minutes.

It has been shown that silicic acid or hydrated silica in a sol as acid as this is positively charged (55). Sodium sulfate should, therefore, be more effective than the chloride, because of the divalent negative ion. It is actually less effective and both are extremely ineffective if they are really acting to coagulate the hydrated silica.

We must conclude, therefore, either that here we have a very unusual type of coagulation of a sol, or that the setting of a silicic acid gel is not a coagulation at all, but occurs by some totally different process.

(2) Structure formed by a mat of fine crystals. Gels such as the myricyl alcohol of Buchner (10) are known, which undoubtedly consist of a mat of fine crystals. They are interlaced or tangled mechanically, and retain their water by capillarity.

It has been suggested many times that the silica in silicic acid gels is in the form of silica crystals. LeChatelier (53) reported that he polished metal by rubbing with silicic acid gel, concluding from this that the gel consisted of anhydrous silica and water, but Bancroft (2) has observed that the pressure used in polishing, or the heat generated, might have caused a dehydration of some of the hydrated silica. The data of Krejci and Ott (46), who found, by x-ray analysis, a cristobalite pattern in freshly prepared silicic acid gels, should be considered seriously. Pascal's (64) magnetic analysis, also, must be considered. His data indicated a complete absence of ortho-, meta-, or pyro-silicic acid molecules in the gel, but did indicate silica and water.

Many observers have claimed to show the presence of definite silicic acids, or definite hydrates of silica, in the gel. This has already been discussed, the references for definite hydrates being represented by Tschermak's paper. The evidence against the existence of definite silicic acids,

represented in this paper by van Bemmelen, Pascal, and Krejci and Ott, has been cited. A careful perusal of the literature will convince the reader of the strong position held by the opposition. It appears quite safe to believe that, whatever the structure may be, silicic acid gels do not consist of mats of crystals of simple silicic acids.

One property possessed by these crystal mat gels is that of thixotropy (20), namely, the ability of the gel to be liquefied by some disturbance, usually by shaking, and then to reset, apparently forming the same structure that it possessed before the disturbance. While a silicic acid gel passes through a period where it may be broken apart, after which it will knit together again, this is not true thixotropy, since the final gel does not knit itself again if it is broken into lumps after it has set. The lumps will remain separate, either under water, which has been added, or in the presence of the liquid due to syneresis. In addition, it proved impossible to liquefy silicic acid gel by the use of ultrasonic waves (21), although gels showing thixotropy were easily liquefied.

It is worth noting one piece of contrary evidence. In washing silicic acid gel very thoroughly, Hurd and Griffeth (36) broke the gel into a very fine suspension by means of a high-speed beater in an excess of distilled water. When the suspended material had settled, it was found to knit together into a firm but fairly weak structure. This can not be considered as ordinary thixotropy.

(3) *Polysilicic acid fibrillar theory.* This theory suggests that a silicic acid gel consists of an interlaced fibrillar or brush heap structure consisting of very large polysilicic acid molecules, the spaces being filled by liquid. The structure is produced by condensation (41), water being split out between two simpler silicic acid molecules to form a more complex structure (35). The polysilicic acid structure is probably very heavily hydrated.

There appears to be little doubt of the formation of simple silicic acid molecules by the reaction of sodium silicate with an acid or by the hydrolysis of silicon tetrahalides or of an alkyl ester of orthosilicic acid. The low molecular weight of the silicic acid in the freshly formed sol has been discussed in this paper under the properties of the sol of hydrated silica (27, 72), the significant point being that, although an apparent molecular weight of about 100 was found in the fresh sol, this value increased to something over 8000, after which experimental error made calculations useless. The ease with which the silicic acid first formed passes through a dialyzer membrane has been mentioned, also the fact that this ability is soon lost. The albumin test of Mylius and Groschuff (59), showing low molecular weight in freshly formed sols of silicic acid, has been cited. They found that the sol, upon standing, changed from the simple α-silicic

acid to the very complex β-silicic acid. All of this evidence supports the theory that a simple monosilicic acid is first formed.

Mylius and Groschuff suggested that their β-silicic acid consisted of very large molecules, formed by condensation of the simple silicic acids first formed. This condensation is analogous to the organic reaction in which water is split out from the two hydroxyl groups of neighboring molecules, resulting in a larger molecule held together by the common oxygen atom. As this procedure continues (31), we picture the formation of more and more complicated structures, causing, ultimately, the complete immobilization of the fluid, which Ostwald says is the most important characteristic of a gel. The gel has now set.

This interconnected branched polysilicic acid structure is almost certainly heavily hydrated. It also holds the fluid in its structure by capillarity. This structure explains, better than any other, the properties of silicic acid gels (32).

This theory is in agreement with the evidence that the silicic acid, when first formed, is in the form of simple molecules, and that the molecular weight increases to very large values. The molecules first formed are undoubtedly quite soluble, but as they condense the resultant product becomes quite insoluble.

The insensitivity to electrolytes is explained. Such a condensation process should be affected very little by the presence of the ions of ordinary salts. The sensitivity to hydrogen and hydroxyl ions is of a different type, and will be explained later.

The heavily hydrated polysilicic acid threads do not become large enough, nor are they of sufficient density, to be visible in the microscope.

The absence of any increase in electrical resistance is understandable, in the light of this theory. While, with the cellular theory, there should be an increase in resistance because of the membranes through which the ions must pass, here the structure remains reasonably open, the passages being continuous.

The measurements of the diameter of the "pores" in the gel by Zsigmondy (81) and by Anderson (1), already quoted, of $5m\mu$ and less, are of about the correct order of magnitude to accord with this theory.

As the gel forms the condensation process continues, undoubtedly, beyond the empirical time, which we term the time of set. The structure already having reached sufficient solidity to set, that is, to pass from the liquid stage to a semisolid stage, any further contraction should squeeze out fluid through the capillaries. This process is what we call syneresis. The tension set up has been commented on by Holmes (30) and others.

The fact that the gel is not thixotropic adds a considerable support to this theory. A gel formed of loose contacts between crystals should be

liquefied, if shaken. The silicic acid gel, because of its firm bonds, which are due to its condensed structure, is not easily broken, even by ultrasonic waves. If it is broken up after it has set, it will not knit together. If it is still in the process of vigorous condensation and it is torn apart, it will easily knit together. Probably, in the very thorough disruption of the structure by Hurd and Griffeth (36), enough of the bonds were broken so that the gel did go through some degree of condensation after settling to the bottom.

This theory offers an explanation of the fact that such a gel retains its proportions if allowed to evaporate fluid in the open. The fluid can come out through the pores to the outside, causing a general shrinkage throughout. When the gel has become well dried, however, the water in the capillaries becomes replaced by air, although the capillaries have shrunk from their original size. This occurs when the water content is from 1.5 to 3.0 moles per mole of silica.

When a well-dried gel is moistened with water it will crack apart, often violently, snapping into pieces. The gel has apparently swelled on the outside before water could penetrate the interior. The strain bursts the lump into pieces.

A structure of this fibrous brush heap character should possess elasticity, as does the silicic acid gel. A distortion should cause a change in shape of the filaments, with an increasing resistance. It is apparently not a lengthening of each filament, but rather a straightening out of irregular chains. When these are straightened out, the structure breaks. It is known that silicic acid gel has a low elastic limit, which is reached, apparently, when most of the filaments have straightened out.

While it is true that the cellular theory presents a somewhat better structure for holding the fluid in the gel, and while some evidence favors the crystal mat theory, we can see that the greater weight of evidence favors the polysilicic acid fibrillar theory. It will be worthwhile, therefore, to present evidence for a reasonable mechanism by which this polysilicic acid structure can be built up.

IX. THE MECHANISM OF CONDENSATION

From the evidence available and from some new data as yet unpublished, we can present a clear and reasonable picture of the mechanism involved in the condensation of silicic acid to form a polysilicic acid structure, resulting in the formation of a silicic acid gel. To do this, we assume: (1) That a monosilicic acid is formed in the first step of the process, or perhaps more correctly, silicon hydroxide. (2) That this acid, or hydroxide, is amphoteric, giving either hydrogen or hydroxyl ions. (3) That condensation occurs when the positive and negative ions containing the silicon come into contact. (4) That water remains combined, or adsorbed, in the structure.

We may now discuss these four assumptions:

(*1*) We shall assume that the first premise is admitted. The low molecular weight and ability to pass through the dialysis membrane have been cited.
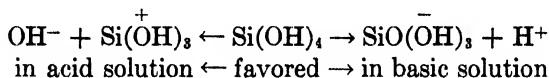
(*2*) The amphoteric character of the silicic acid has been mentioned by Willstätter, Kraut, and Lobinger (80), although it has been tacitly assumed by anyone who has spoken of the condensation mechanism. A clear statement was given by Treadwell and König (73). It is probably impossible to prove this assumption, as it has been found very difficult to measure the ionization constants of any of the well-recognized amphoteric hydroxides.[1]

It will probably be impossible to measure accurately either the acid or basic ionization constants of silicon hydroxide, which, when formed, apparently immediately begins condensation. Treadwell has given what he believes is a reliable value for the acid ionization constant,—namely, $K_1 = 2 \times 10^{-10}$. The great amount of data on the pH of sols of hydrated silica is very confusing, complicated as it is by the presence of impurities, by the age of the sol, and by the method of measurement. What is needed is the pH of a pure sol of the monosilicic acid, measured at the instant of formation. Such data are not available. The only thing of which we may feel certain is that the purest sol, prepared by Kargin and Rabinovich (42) by the oxidation of silane by ozonized oxygen, gave a pH of 7.0, but this material had had ample time for condensation. The data of other observers (67, 9) showed the reaction of a weak acid such as would be expected from Treadwell's constants. The acid ionization is apparently somewhat stronger than the basic ionization.

It is apparently well established that the particles in a sol of hydrated silica are positive in strongly acid solution, but that they become negative in weakly acid, neutral, and basic solution. It has also been observed that the so-called isoelectric point changes with the age of the sol (26). While some difficulty was experienced in explaining this on the basis of the adsorption of ions from the solution, it is very easily explained on the assumption that we have an amphoteric compound. In strongly acid solution the acid ionization of the silicon hydroxide is very strongly repressed, and few silicic acid anions are present. This would be equally true of the condensed acid. The basic ionization would be much increased and most of the silicon would be in the form of the cations. As the acidity of the solution is decreased, leaving lower and lower concentration of hydrogen ions, the acidic type of ionization would be increased and, because the acidic type probably occurs more easily than the basic type, would

[1] Although the Landolt-Bornstein Tables give ionization constants for amphoteric organic electrolytes, none are given for the inorganic amphoteric hydroxides.

equal the basic type even in slightly acid solutions.   The particles which were measured were probably condensed, since the charge on the particles was determined by cataphoresis.   The particles were thus electrically neutral in slightly acid solution where the two types of ionization, occurring in different parts of the same large particle, left it neutral.   In basic solution the acidic type of ionization would be much increased and most of the particles would be negative.   The process is shown for the simplest silicon hydroxide.

$$OH^- + Si\overset{+}{(OH)_3} \leftarrow Si(OH)_4 \rightarrow SiO\overset{-}{(OH)_3} + H^+$$
in acid solution $\leftarrow$ favored $\rightarrow$ in basic solution

The condensed acid is certainly ionized to a much smaller degree than the monosilicic acid, which some observers (57) claim is a reasonably strong acid.   The final product of condensation of the purest silicic acid prepared (42) gave a pH about 7.0, and is probably ionized to a very slight degree. It must be at least very slightly ionized in order that sodium hydroxide may dissolve the gel as it does.

Grundmann's (26) observation that the isoelectric point shifted in a given sol of hydrated silica is interesting.   He found that the particles tended toward a more negative charge as the sol became older.   Apparently, with the larger polysilicic acid molecules, the acidic ionization is decreased less than the basic ionization.   It is well known that silicic acid gel is soluble in or, perhaps better, is peptized by alkali, indicating that the acidic type of ionization is still present in the gel.

(3) Condensation of this type occurs by the splitting out of water from two molecules containing OH groups.   This is equivalent to the following:
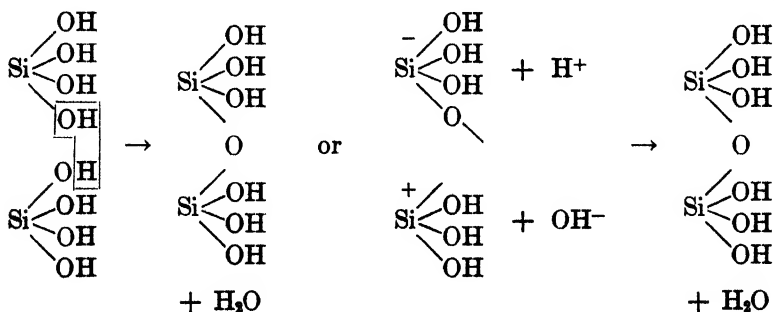
Theoretically such a process should occur more readily if the number of positive and negative ions [$Si\overset{+}{(OH)_3}$ and $SiO\overset{-}{(OH)_3}$] containing silicon were of the same order of magnitude, and if collisions occurred more frequently.

The second idea agrees with the fact, already noted, that the same gel mixture will set more rapidly the higher the temperature. The writer and his coworkers (37, 38) have determined the energy of activation to be about 17,000 calories.

The quantitative relation between time of set and the hydrogen-ion concentration was found by Hurd, Raymond, and Miller (39) for acid gel mixtures. The time of set is a linear function of the hydrogen-ion concentration down to a minimum at about pH = 8.0. This substantiates the idea that the condensation occurs more readily when the two kinds of ions containing the silicon are present in concentrations of about the same order of magnitude.

Measurements of the relation between time of set and the hydrogen-ion concentration in alkaline gel mixtures have proved very difficult, owing to the fact that the hydrogen-ion concentration changes as the gel mixture proceeds toward setting. The shift in the hydrogen-ion concentration in the poorly buffered solutions produced by mixing a solution of sodium silicate with insufficient hydrochloric acid to neutralize it is always toward lower hydrogen-ion concentrations (34). In other words, at first the monosilicic acid formed is enough of an acid to contribute a measurable concentration of hydrogen ions, but as condensation proceeds the polysilicic acids are less and less ionized, resulting in a shift toward lower hydrogen-ion concentration. This net action as an acid is the result of two factors,—(1) that the acidic ionization of silicon hydroxide is greater than the basic ionization and (2) that the basic solution encourages the acidic type of ionization.

Recent measurements obtained in this laboratory, but as yet unpublished, have shown that the time of set in these basic mixtures is nearly proportional to the hydroxyl-ion concentration. Special precautions were used to prevent the shift of hydrogen-ion concentration.

The influence of non-electrolytes upon the time of set doubtless lies in the fact that they have some effect, though not a large one, upon the ionization of the silicon hydroxide.

The fact that very little thermal change occurs as the gel sets has been mentioned (74) and also that this result was unexpected. The fact, however, is entirely in agreement with the theory that is being discussed. The condensation has been occurring steadily since the monosilicic acid was formed in the first reaction. The thermal effect, if measurable, would have been spread out over the whole time and no sudden evolution of heat could be expected as the last of the process was occurring, namely, as the gel set. The process of condensation also includes the ionization of the silicic acids, which would almost nullify the heat produced by the condensation.

Our theory, then, shows reasonable agreement with the facts observed. It presents ideas which may subsequently be tested further by experiment.

(4) While it is perhaps not possible to prove that water remains either chemically combined or strongly adsorbed by the filamentous structure, the facts point strongly toward such a condition.   van Bemmelen's observation that from 0.5 to 1.0 mole of water per mole of silica remained very strongly attached to the silica and could be removed only by vigorous heating, is significant.   The idea of free and bound water has already been mentioned.

Undoubtedly, when a silicic acid gel is subjected to a drying process, the free water in the capillaries is the first to escape.   This causes a shrinkage of the capillary diameters and compresses the fibrous structure.   When the fibrous structure can contract no more, a condition which occurs, apparently, when less than 3 moles of water are present per mole of silica, the water still in the capillaries evaporates, leaving air in the capillaries with about 1 mole of water per mole of silica in the structure.

X. SUMMARY

A review has been given of some of the significant properties of hydrosols of silica and of silicic acid gels.   Methods of preparation have been discussed.

The process of the setting of the sol to form a gel has been examined, particularly in regard to conditions affecting the time of set.

The several theories of gel structure have been examined critically, in regard to their application to the formation of silicic acid gels.

The evidence favors the fibrillar theory for gel structure.

A mechanism for the formation of this fibrillar structure is described. A monosilicic acid is first formed in the sol.   This condenses, owing to the amphoteric nature of the hydroxide of silicon.   The influence of various factors upon this process is discussed, chiefly the hydrogen-ion and hydoxyl-ion concentration and the temperature.   Long chains of condensed polysilicic acids are formed.

These gels are called silicic acid gels, not because we believe that any simple silicic acid is present in the final gel, but because it appears certain that the starting material is a monosilicic acid.

REFERENCES

(1) ANDERSON, J. S.: Z. physik. Chem. **88**, 191 (1914).
(2) BANCROFT, W. D.: Applied Colloid Chemistry, p. 242.   McGraw-Hill Book Co., New York (1921).
(3) VAN BEMMELEN, J. M.: Z. anorg. allgem. Chem. **59**, 225 (1908).
(4) BERZELIUS, J.: Ann. chim. phys. [2] **14**, 363 (1820).
(5) BHATNAGUR, S. S., AND MATHUR, K. K.: Kolloid-Z. **30**, 368 (1922).

(6) Bogue, R. H.: The Theory and Application of Colloidal Behavior, p. 573. McGraw-Hill Book Co., New York (1924).
(7) Bradfield, R.: J. Am. Chem. Soc. 44, 965 (1922).
(8) Brintzinger, H , and Brintzinger, W.: Z. anorg. allgem. Chem. 196, 44 (1931).
(9) Brintzinger, H., and Troemer, B.: Z. anorg. allgem. Chem. 181, 237 (1929); 159, 256 (1927).
(10) Buchner, E. H.: Rec. trav. chim. 42, 787 (1923).
(11) Bütschli, O.: Untersuchen uber Strukturen. Leipzig (1898).
(12) Djatschkowski, S. J.: Kolloid-Z. 51, 316 (1930).
(13) Ebelmen, M.: Ann. chim. phys. [3] 16, 129 (1846).
(14) Ebler, E., and Fellner, M.: Ber. 44, 1915 (1911).
(15) Fells, H. A., and Firth, J. B.: J. Phys. Chem. 29, 241 (1925).
(16) Ferguson, J., and Applebey, M. P.: Trans. Faraday Soc. 26, 642 (1930).
(17) Flade, F.: Z. anorg. allgem. Chem. 82, 173 (1913).
(18) Flemming, W.: Z. physik. Chem. 41, 427 (1902).
(19) Fremy, R.: Ann. chim. phys. [3] 38, 314 (1853).
(20) Freundlich, H.: Kolloid-Z. 46, 289 (1928).
(21) Freundlich, H., Rogowski, F., and Söllner, K.: Kolloid-Beihefte 37, 223 (1933).
(22) Gaunt, H., and Usher, F. L.: Trans. Faraday Soc. 24, 32 (1928).
(23) Ghosh, S., and Dhar, N. R.: J. Phys. Chem. 33, 1905 (1929).
(24) Graham, T.: Ann. Physik 190, 187 (1861).
(25) Grimaux, E.: Compt. rend. 98, 1434 (1884).
(26) Grundman, W : Kolloid-Beihefte 18, 197 (1923).
(27) Gruner, E., and Elöd, J.: Z. anorg. allgem. Chem. 203, 317 (1932).
(28) Hatschek, E.: Trans. Faraday Soc. 12, 17 (1916).
(29) Holmes, H. N.: J. Phys. Chem. 22, 510 (1918).
(30) Holmes, H. N., Kaufmann, W. E., and Nicholas, H. O.: J. Am. Chem. Soc. 41, 1329 (1919).
(31) Hurd, C. B.: Paper presented before the Division of Colloid Chemistry, at the Meeting of the American Chemical Society, April, 1937.
(32) Hurd, C. B.: J. Phys. Chem. 40, 21 (1936); Sigma Xi Quarterly 26, 28 (1938).
(33) Hurd, C. B., and Carver, D. H.: J. Phys. Chem. 37, 321 (1933).
(34) Hurd, C. B., Frederick, K. J., and Haynes, C. R.: J. Phys. Chem. 42, 85 (1938).
(35) Hurd, C. B., Fiedler, W., and Raymond, C. L.: J. Phys. Chem. 41, 553 (1937).
(36) Hurd, C. B., and Griffeth, R. L.: J. Phys. Chem. 29, 1155 (1935).
(37) Hurd, C. B., and Letteron, H. A.: J. Phys. Chem. 36, 604 (1932).
(38) Hurd, C. B., and Miller, P. S.: J. Phys. Chem. 36, 2194 (1932).
(39) Hurd, C. B., Raymond, C. L., and Miller, P. S.: J. Phys. Chem. 38, 663 (1934).
(40) Hurd, C. B., and Swanker, H. J.: J. Am. Chem. Soc. 55, 2607 (1933).
(41) Jordis, E.: Z. anorg. Chem. 44, 200 (1905).
(42) Kargin, V. A., and Rabinovich, A. J.: Trans. Faraday Soc. 31, 284 (1935).
(43) Karsten, C. J. B.: Pogg. Ann. 6, 351 (1826); Ann. Physik 82, 351 (1826).
(44) Katz, J. R.: Kolloid-Beihefte 9, 1 (1917).
(45) Khalizev, A. A.: J. Russ. Phys. Chem. Soc. 61, 1233 (1929).
(46) Krejci, L. J., and Ott, E.: J. Phys. Chem. 35, 2061 (1931).
(47) Krishnamurti, K.: Proc. Roy. Soc. (London) A122, 76 (1929).
(48) Kröger, M.: Kolloid-Z. 30, 16 (1922).
(49) Kuhn, A.: Kolloid-Z. 46, 299 (1928).

(50) LANGMUIR, I.: Communication to the author.
(51) LANGLOIS, M.: Ann. chim. phys. [3] **53**, 331 (1858).
(52) LASKIN, E.: Kolloid-Z. **45**, 129 (1928).
(53) LeCHATELIER, H. L.: La silice et les silicates, p. 76 (1914).
(54) LENHER, V.: Z. physik. Chem. **53**, 351 (1905).
(55) LOSENBECK, K.: Kolloid-Beihefte **16**, 27 (1922).
(56) MASCHKE, O.: Ann. Physik **222**, 90 (1872).
(57) MUKHERJEE, I : Kolloid-Z. **67**, 178 (1934).
(58) MUNRO, L. A., AND ALVES, C. A.: Can. J. Research **B15**, 353 (1937).
(59) MYLIUS, F., AND GROSCHUFF, E.: Ber. **39**, 116 (1906).
(60) NAGELI, K. VON: Pflanzen Physiologischen Untersuchen. Zurich (1858).
(61) OSTWALD, W.: Kolloid-Z. **46**, 248 (1928).
(62) OSTWALD, W., AND FISCHER, M. H.: An Introduction to Theoretical and Applied Colloid Chemistry, p. 102. John Wiley & Sons, New York (1917).
(63) PAPPADA, N., AND SADOWSKY, C.: Kolloid-Z. **6**, 292 (1910).
(64) PASCAL, P.: Compt. rend. **175**, 184 (1922).
(65) PRASAD, M., AND HATTIANGADI, P. B.: J. Indian Chem. Soc. **6**, 653 (1929); **6**, 893 (1929); **7**, 341 (1930).
(66) PRASAD, M., MEHTA, S. M., AND DESAI, J. B.: J. Phys. Chem. **36**, 1324 (1932).
(67) RABINOVICH, A. J., AND LASKIN, E.: Z. physik. Chem. **134**, 387 (1928).
(68) RAY, R. C., AND GANGULY, P. B.: J. Phys. Chem. **35**, 596 (1931); **34**, 352 (1930).
(69) SCHWARZ, R.: Kolloid-Z. **28**, 77 (1921).
(70) SCHWARZ, R.: Z. Elektrochem. **32**, 415 (1926).
(71) THOMAS, A. W.: Colloid Chemistry, p. 145 et seq. McGraw-Hill Book Co., New York (1934).
(72) TREADWELL, W. D.: Trans. Faraday Soc. **31**, 297 (1935).
(73) TREADWELL, W. D., AND KONIG, W.: Helv. Chim. Acta **16**, 54 (1933).
(74) TREADWELL, W. D., AND WIELAND, W.: Helv. Chim. Acta **13**, 842 (1930).
(75) TSCHERMAK, G.: Z. anorg. allgem. Chem. **63**, 230 (1914).
(76) WALDEN, P.: Kolloid-Z. **6**, 233 (1910); **9**, 145 (1911).
(77) VON WEIMARN, P. P.: Kolloid-Z. **46**, 356 (1928).
(78) VON WEIMARN, P. P.: Gels and Gelatinous Precipitates, etc. Department of Commerce and Industry, Osaka, Japan (1928).
(79) WEISER, H. B.: The Hydrous Oxides. McGraw-Hill Book Co., New York (1926). Inorganic Colloid Chemistry, John Wiley & Sons, New York (1935).
(80) WILLSTATTER, R., KRAUT, H., AND LOBINGER, K.: Ber. **58B**, 2462 (1925).
(81) ZSIGMONDY, R.: Z. anorg. allgem. Chem. **71**, 356 (1911).

THE STRUCTURE OF PROTEINS IN RELATION TO BIOLOGICAL PROBLEMS[1]

MAX BERGMANN

Laboratories of The Rockefeller Institute for Medical Research, New York, New York

There are in protein chemistry two fundamental theories which have been accepted for many years. One is the well-known peptide theory of Emil Fischer (17) and of Hofmeister (19). According to this theory the molecule of a protein is supposed to be constructed of a large number of amino acids which are combined one by one through peptide bonds, thus forming a long chain containing many CO—NH groups or peptide bonds. We know about twenty-five amino acids to be constituents of proteins. The various proteins are supposed to differ with regard to the length of the peptide chain and the relative content and sequence of the individual amino acid residues. Fischer has emphasized that there is an almost infinite number of possible sequences of amino acid residues. For example, it was calculated that thirty amino acid residues, among them eighteen of different nature, can give rise to the existence of 1.28×10^{27} different proteins (18).

The second general theory concerns the enzymic digestion of proteins. Proteins have been supposed to be degraded, step by step, into peptones, polypeptides, dipeptides, and eventually amino acids. It is assumed that each step is performed by a special enzyme or group of enzymes (22, 16). The first step, which consists in the degradation of the original high molecular proteins, is attributed to enzymes called proteinases, such as pepsin or trypsin. None of these proteinases was found capable of digesting simple peptides,—either natural or synthetic peptides. On the other hand, it was observed that the enzymes that attack simple peptides could not digest high molecular proteins. There was considerable discussion (20, 21) about the question as to how to reconcile the peptide theory with the fact that proteins are digested by enzymes which do not attack the peptide bonds of all the known low molecular polypeptides. Until very recently it has been assumed that proteinases are restricted to high molecular

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[1] The text of this paper, which is based principally on results obtained in this laboratory, is presented as delivered, by invitation, at the Seventh National Organic Chemistry Symposium of the American Chemical Society, December 29, 1937, at Richmond, Virginia.

substrates. On the other hand, it has repeatedly been suggested that proteins may contain large numbers of linkages that differ from peptide bonds and may be the points at which pepsin, trypsin, and other proteinases attack the protein molecule. None of these hypotheses has found sufficient experimental support.

And, indeed, no experimental support could have been expected. If proteinases are in reality capable of attacking only high molecular proteins or certain special linkages found in high molecular proteins, it is obviously futile to expect to obtain any experimental evidence on the specificity of proteinases by the use of simple synthetic peptides. However, if we reëxamine our knowledge regarding proteins, there arises some doubt whether the original premise of our argument is correct. The disparity in molecular weight is not the sole difference between proteins and peptides. Another significant difference lies in the fact that proteins contain practically no free α-amino or free α-carboxyl groups, while peptides do contain such groups. The presence of these ionizable groups should influence decisively the polar character of the peptide molecule and of its peptide bonds, thus affecting the enzymic digestibility. Consequently we synthesized peptide-like substances of low molecular weight, which had neither free α-carboxyl nor α-amino groups and conformed to the general scheme

$$R' \cdot CO-NH \cdot CHR'' \cdot CO-NHR'''$$

To our satisfaction, certain of these protein models were found to be easily digested by crystalline trypsin (8), others by crystalline chymotrypsin (6) and heterotrypsin (6, 12), and still others by the intracellular proteinases papain (13, 14, 15), cathepsin, and bromelin (7). For each of the representative proteinases, with the exception of pepsin, we were thus able to synthesize numerous substrates; a few of them are reported in table 1.

Since the structure of these substrates may be varied in many ways, there is no longer any obstacle to a detailed investigation of the specificity of each of these enzymes. It was found that each proteinase has its individual specificity and therefore its individual substrates. These synthetic substrates are the long-needed tools for a characterization of the specific nature and the exact quantity of proteinases contained in crude biological preparations and for an investigation of the homogeneity and the kinetics of purified enzymes. As an example of the usefulness of the synthetic substrates I should like to mention the discovery that commercial pancreatin contains large quantities of a hitherto unknown tryptic enzyme which has been designated heterotrypsin.

As another result of the study of synthetic protein models it must be mentioned that the digestive action of trypsin, pepsin, and other proteinases does not stop with the formation of peptones but may, in part, proceed

to the formation of simple peptides or even amino acids. How far the digestion of a protein proceeds is a question not of the molecular size but of the structure of the intermediate products. The presence or absence of α-amino or α-carboxyl groups and the nature and sequence of side chains direct the course and limit the extent of the digestion. Very remarkable indeed is the highly differentiated specificity of our various digestive proteinases as illustrated by trypsin, chymotrypsin, and heterotrypsin. It is generally assumed that the task of digestion is a complete breakdown of food proteins into amino acids. It appears, however, as though the digestive tract takes special precautions in order to conduct the digestion along certain structural lines.

Table 1 also reports the fact that all the proteinases are specifically adapted to the splitting of peptide bonds. Therefore there is no doubt that the digestive action of these enzymes on proteins is performed at the peptide bonds. We no longer have to fear that proteins contain large

TABLE 1

Substrates of proteinases

ENZYME	SUBSTRATE
All enzymes	R'·CO—NH·CHR''·CO—NHR'''
Trypsin	Benzoyl-*l*-arginine amide
Chymotrypsin	Benzoyl-*l*-tyrosylglycine amide
Heterotrypsin	Benzoylglycyl-*l*-lysine amide
Papain	Benzoylglycine amide
Cathepsin	Carbobenzoxy-*l*-leucylglycylglycine
Bromelin	Carbobenzoxyglycyl-*l*-glutamylglycine amide

numbers of linkages of unknown nature, but can without reservation consider the peptide bonds to form the essential links connecting the amino acid residues inside a protein molecule.

Through our experiments with artificial substrates we have killed two birds with one stone: we have arrived at a new concept of enzymatic proteolysis and, simultaneously, we have strengthened the general validity of the peptide theory—or, at least, of one claim of the peptide theory. We can now be certain that proteins have the structure of peptide chains. However, within the peptide scheme of proteins there are still a number of variables, such as (*1*) the length of the peptide chain expressed in the total number of amino acid residues contained in one molecule of a protein, and (*2*) the ratio and the sequence of the individual amino acid residues contained in that protein molecule. By the variation of the total number, the ratio, and the sequence of the amino acid residues, there is possible, theoretically, an infinite number of proteins. Actually, it was found that only a

limited number of these variations are realized in nature (9, 10, 11). This important fact is demonstrated in tables 2 and 3. In table 2 there is reported the analysis of several constituents of cattle blood globin. In table 3 there are found the numbers of amino acid residues per molecule in four proteins of rather different physiological significance, such as the albumin of the chicken egg, the globin and the fibrin of cattle blood, and

TABLE 2

The number of amino acid residues per molecule of cattle blood globin

1	(2)	(3)	(4)	(5)	(6)
AMINO ACID RESIDUE	WEIGHT	RESIDUE WEIGHT	GRAM-EQUIVA-LENTS PER 100 GRAMS OF GLOBIN	RECIPROCAL FRACTIONAL VALUE	RATIO (NUMBER OF INDIVIDUAL RESIDUES PER MOLECULE)
	per cent				
Lysine	7 01	128	0 0546	16	36
Histidine	6.54	137	0.0478	18	32
Aspartic acid	5 53	115	0 0479	18	32
Glutamic acid	3.07	129	0 0239	36	16
Tyrosine	2 97	163	0 0182	48	12
Proline	1.77	97	0.0182	48	12
Arginine	2 78	156	0.0181	48	12
Cysteine	0 47	103	0 0046	192*	3*
Average		115 5	0.865	1	576

* Calculated as cysteine.

The percentage found for an individual amino acid residue (column 2), divided by the weight of this residue (column 3), gives the number of gram-equivalents of this residue found per 100 grams of globin (column 4).

The average weight of all amino acid residues in globin is 115.5. Therefore, 100 grams of globin contains $100/115.5 = 0.865$ gram-equivalent of an average amino acid residue.

Lysine comprises $0.0546/0.865 = 1/16$ of all the constituent residues of globin; histidine comprises $0.0478/0.865 = 1/18$; etc. (column 5).

The ratios in column 6 are obtained directly from column 4.

By multiplying a value of column 6 by the corresponding value in column 5, one obtains the total number of amino acid residues contained in one molecule of globin. Globin thus contains $36 \times 16 = 576$ residues of an average weight of 115.5. Globin therefore has a molecular weight of $576 \times 115.5 = 66,520$. This is a minimum value. The correct value may be a whole number multiple thereof.

the fibroin of the silkworm fiber. Time does not permit a description of the newer and relatively simple methods which enable us to perform the estimation of quite a number of amino acids with a high degree of precision (11, 3, 1, 2).

When we analyze a protein as, for example, cattle hemoglobin, our analytical methods enable us to find that one molecule of this protein

contains thirty-six lysine units, and that these units are one-sixteenth of the total number of units contained in one molecule of cattle hemoglobin. When the number of individual units (N_i) and the reciprocal fractional value (F_i) are multiplied by each other, we find the total number of amino acid residues in one protein molecule, as shown in equation 1 of table 4. The values reported in table 3 for the amino acid content of four proteins

TABLE 3

The number of amino acid residues (units) per molecule of various proteins

AMINO ACID	CATTLE GLOBIN	CATTLE FIBRIN	CHICKEN EGG ALBUMIN	SILK FIBROIN
All amino acids .	$2^6 \times 3^2$	$2^6 \times 3^2$	$2^5 \times 3^2$	$2^5 \times 3^4$
Arginine	$2^2 \times 3^1$	$2^5 \times 3^0$	$2^2 \times 3^1$	$2^2 \times 3^1$
Lysine	$2^2 \times 3^2$	$2^4 \times 3^1$	$2^2 \times 3^1$	$2^2 \times 3^0$
Histidine	$2^5 \times 3^0$	$2^2 \times 3^1$	$2^2 \times 3^0$	$2^0 \times 3^0$
Aspartic acid	$2^5 \times 3^0$	$2^5 \times 3^0$	$2^4 \times 3^0$	
Glutamic acid	$2^4 \times 3^0$	$2^3 \times 3^2$	$2^3 \times 3^2$	
Glycine				$2^4 \times 3^4$
Alanine				$2^3 \times 3^4$
Tyrosine	$2^2 \times 3^1$		$2^3 \times 3^0$	$2^1 \times 3^4$
Proline	$2^2 \times 3^1$	$2^5 \times 3^0$		
Tryptophane		$2^1 \times 3^2$		
Cysteine	$2^0 \times 3^1$	$2^0 \times 3^2$	$2^2 \times 3^0$	
Methionine		$2^2 \times 3^1$	$2^2 \times 3^1$	
Molecular weight	66,520	69,300	35,700	217,700

TABLE 4

General formulas regarding the number of units per molecule of the proteins of table 3

(1) $N_i \times F_i = N_t$

(2) $N_t = 2^m \times 3^n$, where m and n are positive whole numbers

(3) $N_i = 2^{m'} \times 3^{n'}$ where m', m'', n', and n'' are either zero or positive whole num-

(4) $F_i = 2^{m''} \times 3^{n''}$ bers

(5) $m = m' + m''$

(6) $n = n' + n''$

reveal the surprising fact that N_i and F_i, and therefore N_t, can be expressed by powers of 2 and 3, as shown in the general equations 2, 3, and 4 of table 4. Everyone who is familiar with the history of protein chemistry may feel somewhat amazed on being confronted with a simple stoichiometry of the protein molecule and with numerical rules such as are reported in table 4. Perhaps it would not seem to be superfluous to point out that these rules are not mere hypothetical conceptions but actual experimental results.

The experiments on which these results are based cover, at the present time, only a restricted number of proteins. However, the numerical rules observed are of so pronounced a uniformity that it seems natural to generalize their validity beyond the four proteins which have been discussed. There already exist indications that similar numerical rules hold good for many other natural proteins. As such proteins there may be mentioned collagen (analyzed by Niemann and Stein in this laboratory), elastin (analyzed by Miller and Stein in Dr. Hans T. Clarke's laboratory), and insulin (du Vigneaud). Furthermore, the finding of Svedberg and his collaborators that the particle sizes of many proteins exhibit approximate numerical regularities has been interpreted as pointing to a common plan for the building up of the protein molecules (23).

This common plan has its basis in our equation 2 (table 4). Equation 2 expresses the fact that the molecules of various proteins fall into classes containing a definite number of amino acid units: for example, chicken egg albumin falls into the class with 288 units, cattle blood globin and fibrin into the class with 576 units, and silk fibroin into the class with 2592 units.

If a protein consists exclusively or almost exclusively of amino acid units, then an elementary calculation permits the transformation of the total number of units into the molecular weight of the protein. The chemical analysis reveals not only the total number of units but also their average weight. By multiplying the total number of units by their average weight we get a fairly accurate value of the molecular weight. As in the case of simpler compounds, a molecular weight obtained by chemical analysis is a minimum value and the true value may be a whole number multiple thereof. The molecular weights obtained for the four proteins considered in table 3 are, respectively: 35,700; 66,520; 69,300; and 217,700. Here we find, indeed, a regularity similar to that observed by Svedberg by means of the particle size method. It is apparent, however, that the regularity of the molecular weights is, and can only be, an approximate one. It is quite instructive to compare fibroin with egg albumin. The average residue weight of fibroin is unusually low, since it consists for the most part of small amino acid units; therefore its molecular weight is only six times that of egg albumin, although fibroin has nine times the number of units of egg albumin.

In order to understand the meaning of a molecular weight of a protein just as in the case of a simpler compound, we have to know the kind and the number of its constituents and the structural pattern in which they are arranged. In the case of many natural proteins the number of units is expressed by the numerical rules stated in equations 2 to 4. These rules must have a basis in the structural pattern of the protein,—that is, in the sequence of the amino acid units. These units cannot be distributed at

random. Their sequence must rather be such that it includes by implication the numerical rules found experimentally. There is only one structural principle that fulfills this requirement: it may be illustrated by the example of silk fibroin, since of all the well-known high molecular proteins fibroin has the simplest pattern. Exactly one-half of the constituents of fibroin are glycine residues. This fact may be expressed in the conclusion that every second amino acid residue in the peptide chain of fibroin must be a glycine residue (G):
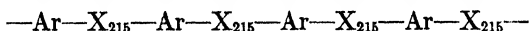
$$-G-X-G-X-G-X-G-X-$$

Every fourth residue in the chain is an alanine residue (A):

$$-A-X_3-A-X_3-A-X_3-A-X_3-$$
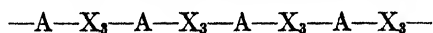
Every sixteenth residue is a tyrosine residue (T):

$$-T-X_{15}-T-X_{15}-T-X_{15}-T-X_{15}-$$
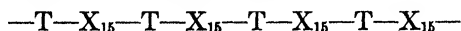
And every two hundred and sixteenth is an arginine residue (Ar):

$$-Ar-X_{215}-Ar-X_{215}-Ar-X_{215}-Ar-X_{215}-$$

When the above four schemes are combined into one, we obtain the following structure of a segment of the silk fibroin molecule representing 432 amino acid residues or one-sixth of the whole molecule: —G—A—G—T—G—A—G—Ar—G—A—G—X—G—A—G—X—[G—A—G—T—G—A—G—X—G—A—G—X—G—A—G—X]$_{12}$—G—A—G—T—G—A—G—X—G—A—G—X—G—A—G—Ar—[G—A—G—T—G—A—G—X—G—A—G—X—G—A—G—X]$_{13}$—. As a general rule, the amino acid residues of a protein molecule may be arranged in such a way that each individual residue repeats itself throughout the protein molecule at constant intervals, i.e., with a regularly recurring frequency. The frequencies are different, in general, with respect to various kinds of amino acid residues of the same molecule. The protein molecule thus contains a number of different, superimposed frequencies. This principle of the superimposed frequencies confers a relatively simple structural pattern upon the giant protein molecule. Living organisms therefore do not achieve the synthesis of the immense number of proteins provided by the peptide theory in its original conception, but seem to synthesize only those proteins that exhibit these simple numerical rules and the pattern of the superimposed frequencies. How is such a limitation in the number and types of naturally occurring proteins to be explained? It seems to me to have its origin in the mechanism of the biological synthesis of protein molecules. As long as we expected to meet in nature every kind of protein provided by the peptide theory in its general, unrestricted form, we had no

indication of the means by which the variety of natural proteins is produced. The discovery of the quantitative rules governing the protein molecule makes the biological synthesis of an individual protein molecule appear as a process which involves a specificity that is both highly delicate and extremely complex. Such specificity phenomena are a clear indication of the operation of an enzymatic process which directs all the steps involved in the synthesis of the special pattern of each individual protein. We have approached this problem experimentally in the belief that in living cells proteinases should direct the synthesis of proteins and should exhibit some kind of specificity hitherto unknown.

It has been supposed for quite a while that proteolytic enzymes may be involved in protein synthesis. A number of investigators—as, for example, Wasteneys and Borsook (26), Taylor (24), and Voegtlin and his collaborators (25)—have studied the changes in substrate concentration, pH, and activation which might be necessary in order to divert the action of those enzymes from protein splitting to protein synthesis. All these investigators had to perform their experiments with very complex mixtures of protein digestion products, the very structure of which was unknown.

Under such experimental circumstances a large number of chemical and physical conditions influence a multitude of different peptide bonds, and the analytical findings are often a summation of many conflicting, partial results. In order to obtain clear-cut results, it is necessary to simplify the experimental conditions fundamentally. Here we were able to use to advantage our finding that the enzymes which attack genuine proteins also act on very simple substrates, provided that these substrates meet the specificity requirements of the enzyme involved.

Our experiments were performed with the best known intracellular proteinase, the papain of the so-called melon tree. It was readily established (4, 5) that such enzymes, when activated, are capable of performing four different types of reaction (table 5).

(1) The hydrolytic effect of papain, which may best be illustrated by the splitting of benzoylglycine amide into benzoylglycine and ammonia, is well known.

(2) The phenyl derivative of the benzoylglycine amide just mentioned is not at all split by papain; on the contrary, it is synthesized from benzoylglycine and aniline when papain is present. Such syntheses, in many cases, reach 100 per cent and proceed with remarkable speed. When the synthesis of benzoylleucine anilide from benzoyl-l-leucine and aniline is performed in a 2 to 3 per cent solution, after 5 minutes the mixture is already solidified by the crystallization of the anilide synthesized. As another example the synthesis of benzoylleucylleucine anilide from benzoylleucine and leucine anilide may be mentioned. Here the enzymic action combines two natural amino acids with each other through a genuine peptide bond.

(3) When benzoylglycine amide is treated with a diluted solution of aniline in the presence of papain, the aniline replaces the amide group with the formation of benzoylglycine anilide.

(4) On the other hand, when a mixture of benzoylleucine and glycine anilide is treated with papain, the benzoylleucine replaces the glycine residue with the formation of benzoylleucine anilide.

Reactions of types 3 and 4 deal with the replacement of one group by another.[2] Such replacement reactions have hitherto not been considered in connection with proteolytic enzymes. And yet they may in many cases complicate the situation when we perform an enzymic digestion of a protein.

<div align="center">

TABLE 5

Reaction types catalyzed by papain

</div>

(1) $C_6H_5 \cdot CO-NH \cdot CH_2 \cdot CO-NH_2 \rightarrow C_6H_5 \cdot CO-NH \cdot CH_2 \cdot COOH + NH_3$

(2) $C_6H_5 \cdot CO-NH \cdot CH_2 \cdot COOH + NH_2 \cdot C_6H_5 \rightarrow$
$$C_6H_5 \cdot CO-NH \cdot CH_2 \cdot CO-NH \cdot C_6H_5$$

$$Bz-NH \cdot \underset{\underset{C_4H_9}{|}}{CH} \cdot COOH + NH_2 \cdot \underset{\underset{C_4H_9}{|}}{CH} \cdot CO-NH \cdot C_6H_5 \rightarrow$$

$$Bz-NH \quad \underset{\underset{C_4H_9}{|}}{CH} \cdot CO-NH \cdot \underset{\underset{C_4H_9}{|}}{CH} \cdot CO-NH \cdot C_6H_5$$

(3) $C_6H_5 \cdot CO-NH \cdot CH_2 \cdot CO-NH_2 + NH_2 \cdot C_6H_5 \rightarrow$
$$C_6H_5 \cdot CO-NH \cdot CH_2 \quad CO-NH \cdot C_6H_5 + NH_3$$

(4) $Bz-NH \cdot \underset{\underset{C_4H_9}{|}}{CH} \cdot COOH + NH_2 \cdot CH_2 \cdot CO-NH \cdot C_6H_5 \rightarrow$

$$Bz-NH \cdot \underset{\underset{C_4H_9}{|}}{CH} \cdot CO-NH \cdot C_6H_5 + NH_2 \cdot CH_2 \cdot COOH$$
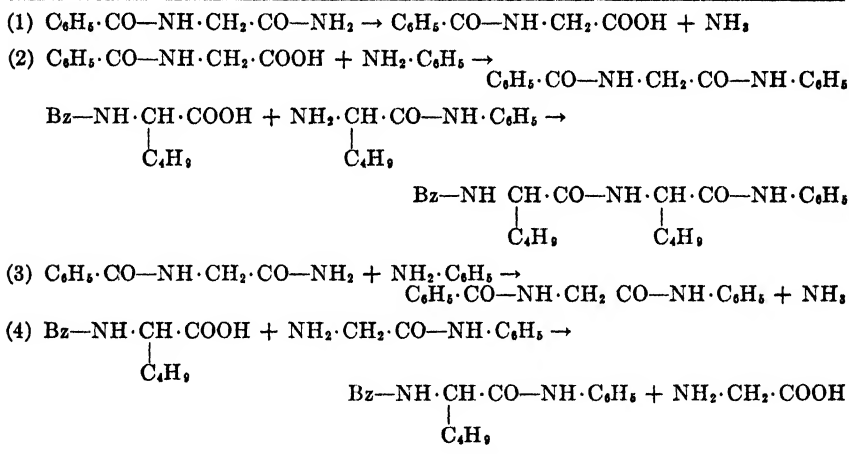
With respect to the problem of the biological synthesis of proteins, our finding that the four types of enzymic reactions described above occur under identical conditions of pH, activation, etc., seems to be of some significance. No longer can it be claimed to be a general rule that hydrolysis occurs at one pH and synthesis at another.

Which one of the four types of reaction discussed above may occur in a living cell at a given moment is determined in the first place by specificity phenomena, that is, by the specificity of the enzyme involved and by the structure of the substrates available. The mutual interdependence between the substrate structure and the specific action of an enzyme may be

[2] It is at present not certain whether replacements of type 4 proceed directly or through some more complex mechanism.

illustrated by the fate of several comparative series of substrates when in contact with an enzyme.

Series A (papain)

Benzoylleucylglycyl|glycine	Hydrolyzed
Benzoylleucyl|leucylglycine	Hydrolyzed

Series A deals with two molecules of identical chain length and identical general type. They differ only with respect to the nature of one aliphatic amino acid residue, and yet this small difference effects the shift of the point of hydrolysis from one peptide bond to another.

Series B (papain)

Benzoylleucine + Leucine anilide → Benzoylleucylleucine anilide
Benzoylleucine + Glycine anilide → Benzoylleucine anilide
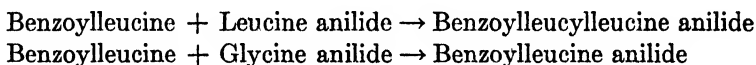
Here we compare two reaction systems of the same type. They differ only in that the first system contains a leucine residue, whereas the second system contains a glycine residue. This difference causes the two substrates to react differently under the influence of papain. The first system undergoes a synthesis, the second system a replacement reaction.

Series C (papain)

Benzoylleucyl|leucylglycine	Hydrolysis
Benzoylleucine + Leucine anilide	Synthesis

The two systems considered in series C contain the same amino acid residues as constituents participating in the enzymic reaction. The two systems differ, however, with respect to substituents outside the sphere of enzymic action. As a result, the two systems react under the influence of papain in opposite directions.

Series D (chymotrypsin)

Benzoyltyrosine amide	No hydrolysis
Benzoyltyrosylglycine	No hydrolysis
Benzoyltyrosyl|glycine amide	Quick hydrolysis
Benzoyltyrosylglycylglycine amide	Very slow hydrolysis

Series D deals with substrates for chymotrypsin. Exactly as in series C, we find remote sections of the molecule influencing the splitting of a given peptide bond.

The various reactions just discussed demonstrate the pronounced specificity of proteinases and, on the other hand, the rather complex nature of

this specificity. By the term "enzymatic specificity" we have usually designated the fact that a relatively slight modification of the substrate may inhibit the enzymatic action. The specificity of proteinases, however, is such that structural alterations of the substrate very often do not inhibit the action of the enzyme, but shift the point of enzymatic attack or alter the type of enzymic reaction. A proteinase is capable of producing a variety of reactions and of reacting on a variety of substrates. Nevertheless, on each substrate it performs in general only one unequivocal reaction. This combination, in a single enzyme, of versatility and unequivocal action may be of the greatest significance in the biological synthesis of individual proteins.

Before we discuss the possible course of such a biological synthesis, there should be mentioned another aspect of the specificity phenomenon, having its basis in the complex nature of the substrate. It lies in the fact, which was mentioned before, that the enzymatic behavior of a peptide bond is frequently influenced by distant sections of the substrate molecule. A peptide bond between two individual amino acid residues is not an independent entity endowed with specific properties of its own. The energy content and the specific nature of a peptide bond are the resultants of the interaction of many sections of the entire substrate molecule. Such an interaction of the various sections of a molecule is common to all kinds of compounds. However, its consequences are very impressive and extremely significant in the synthesis of protein molecules, since here we have to deal with the action of enzymes possessing a highly sensitive specificity and with a reaction sequence consisting of at least hundreds of single steps, each of which offers a great variety of modifications.

Thus, for example, during the synthesis of a fibroin molecule several thousands of peptide bonds are formed. We may visualize this synthesis as consisting of a large number of single steps. A few of them are represented in table 6. Each of these steps means the attachment of an amino acid residue or a peptide residue to the rudimentary fibroin molecule. In the interest of simplicity only the attachment of single amino acid residues is considered in table 6. In each single step of the synthesis the enzyme makes a precise selection from the variety of available amino acids, attaching in one step of the synthesis glycine, in the next step alanine, then glycine, tyrosine, glycine, alanine, and so on. Each step of the synthesis changes the size and the structure of the rudimentary fibroin molecule, and simultaneously the nature of the amino acid to be attached varies also from step to step. The synthesizing enzyme has to act on a different substrate in each single step; by its action in one step it has used up the reaction product of the foregoing step and has synthesized the substrate of the next step.

Thus, according to this picture, the highly organized pattern of a protein molecule is the result of a reaction sequence, consisting of numerous single yet interdependent steps.   It is the capability of the proteinases to perform long sequences of reactions in an unequivocal way that is instrumental in producing the unequivocal pattern of an individual protein.   Neither an enzyme specifically restricted to a single substrate nor an enzyme acting on various substrates in an unspecific manner could produce the unique pattern of an individual protein.   We can explain the formation of proteins only by postulating the presence in living organisms of enzymes capable of acting on a multitude of substrates and having the property of acting on each of these substrates in a sharply defined manner.   The specificity of an individual enzyme predetermines the molecular pattern of the protein synthesized by this enzyme.   The numerical rules governing a protein molecule have their basis in the specificity of the enzyme involved.   Here

TABLE 6

Synthesis of a segment of the fibroin molecule

The symbol R refers to the rudimentary fibroin molecule at a given stage of the synthesis.   The symbols G, A, and T refer respectively to the residues of glycine, alanine, and tyrosine.

R + glycine	→ R·glycine
R·glycine + alanine	→ R G·alanine
R·G·alanine + glycine	→ R G·A·glycine
R·G·A glycine + tyrosine	→ R·G·A·G tyrosine
R·G·A·G·tyrosine + glycine	→ R G·A·G·T·glycine
R G·A G·T glycine + alanine	→ R·G A·G·T·G·alanine
R·G A·G·T G·alanine + glycine	→ R G·A·G·T·G·A·glycine
R·G·A·G T·G A·glycine + arginine	→ R·G·A·G·T·G·A·G·arginine

we arrive for the first time at a physicochemical concept of the predetermination which is an inherent attribute of many phenomena of life.

The question of whether hereditary phenomena are connected with and explained by a transmission of individual proteins has frequently been discussed.   On the basis of the conclusions which we have reached, it seems that the essential substances transmitted from one generation of cells to the next must be enzymes, and that they have to be enzymes gifted with the capability of synthesizing individual proteins by predetermined sequences of specificity reactions.   There is already considerable evidence that proteinases themselves are proteins, or contain proteins as essential molecular constituents.   Therefore the proteinases owe their existence to the preëxistence of other proteinases.   There is, in life, a practically endless sequence of sequence reactions, in which one proteinase synthesizes the next by a predetermined reaction, and so forth.   The sequence breaks

off whenever a proteinase has synthesized a protein that does not possess enzymatic properties.

Will we ever be able to copy *in vitro* the synthesis of natural proteins? I do not know whether we may succeed sooner or later (probably later) in synthesizing proteins with the aid of proteinases and without the coöperation of living cells. However, I am doubtful how much a synthesis of this kind would add to our understanding of protein chemistry and life phenomena. At the present moment it would seem to be of still greater significance that we have available methods to study the composition and the transformations of proteins and the specificity of proteinases with the same precision as in the case of simpler substances and simpler phenomena. Thus we may hope to extract much new information about the numerous physiological and pathological processes that are dependent upon the formation, the presence, or the transformation of proteins.

REFERENCES

(1) BERGMANN, M.: J. Biol. Chem. **110**, 471 (1935).
(2) BERGMANN, M.: J. Biol. Chem. **122**, 569 (1938).
(3) BERGMANN, M., AND FOX, S. W.: J. Biol. Chem. **109**, 317 (1935).
(4) BERGMANN, M., AND FRAENKEL-CONRAT, H.: J. Biol. Chem. **119**, 707 (1937).
(5) BERGMANN, M., AND FRAENKEL-CONRAT, H.: J. Biol. Chem. **124**, 1 (1938).
(6) BERGMANN, M , AND FRUTON, J S : J. Biol. Chem **118**, 405 (1937).
(7) BERGMANN, M., FRUTON, J. S., AND FRAENKEL-CONRAT, H.: J. Biol. Chem. **119**, 35 (1937)
(8) BERGMANN, M., FRUTON, J. S., AND POLLOK, H.: Science **85**, 410 (1937)
(9) BERGMANN, M., AND NIEMANN, C.: J. Biol. Chem **115**, 77 (1936).
(10) BERGMANN, M., AND NIEMANN, C : J. Biol. Chem **118**, 301 (1937).
(11) BERGMANN, M., AND NIEMANN, C.: J. Biol. Chem. **122**, 577 (1938).
(12) BERGMANN, M., AND ROSS, W F.: J. Am. Chem. Soc **58**, 1503 (1936).
(13) BERGMANN, M., ZERVAS, L., AND FRUTON, J. S.: J. Biol. Chem. **111**, 225 (1935).
(14) BERGMANN, M., ZERVAS, L , AND FRUTON, J. S : J. Biol. Chem. **115**, 593 (1936).
(15) BERGMANN, M , ZERVAS, L , AND ROSS, W. F.: J. Biol. Chem. **111**, 245 (1935).
(16) BERTHO, A , AND GRASSMANN, W.: Biochemisches Praktikum, p. 99. Walter de Gruyter and Co., Berlin (1936)
(17) FISCHER, E.: Ber. **39**, 530 (1906).
(18) FISCHER, E.: Untersuchungen über Aminosauren, Polypeptide und Proteine, Vol. II, p. 41. Julius Springer, Berlin (1923).
(19) HOFMEISTER, F.: Naturw. Rundschau **17**, No. 42/43 (1902).
(20) LINDERSTRÖM-LANG, K : Ergeb. Physiol. exptl. Pharmakol. **35**, 415 (1933).
(21) OPPENHEIMER, C.: Die Fermente und ihre Wirkungen, 5th edition, Supplement, p. 611. W. Junk, The Hague (1936).
(22) Reference 21, p. 618.
(23) SVEDBERG, T.: Ind. Eng. Chem., Anal. Ed. **10**, 113 (1938).
(24) TAYLOR, A. E.: J. Biol. Chem. **3**, 87 (1907).
(25) VOEGTLIN, C., MAVER, M. E., AND JOHNSON, J. M.: J. Pharmacol. **48**, 241 (1932).
(26) WASTENEYS, H., AND BORSOOK, H.: Physiol. Rev. **10**, 110 (1930).

THE THEORY OF REVERSIBLE TWO-STEP OXIDATION INVOLVING FREE RADICALS

L. MICHAELIS AND M. P. SCHUBERT

Laboratories of The Rockefeller Institute for Medical Research, New York, New York

In a previous review (9) there was presented the evidence for the existence of free radicals, designated as semiquinones, which are intermediate products formed in organic oxidation–reduction reactions. At that time emphasis was placed on the experimental basis of the theory. Since then, with the accumulation of more actual examples in other laboratories as well as in this one, it has been possible to extend and to simplify the whole underlying theory. Because the importance of the problem has become more generally recognized, it is worth while now to present this theory comprehensively, and to develop it not from the historical but from a purely logical point of view. Since it is the purpose of this review to unify work scattered through various publications (8, 10 to 19, 21) changes have been made in some of the equations, but the equivalence of the new forms with the earlier ones will easily be recognized. Another problem to be discussed in this review is the relation between the equations for this stepwise oxidation and the equations for the stepwise ionization of dibasic acids.

I. THE FUNDAMENTAL REDUCTION PROCESS

If a substance, A, can undergo a reversible reduction by accepting an electron,[1] the process may be represented thus:

$$A + \epsilon \rightleftharpoons A^- \tag{1}$$

[1] List of symbols used:

ϵ = electron,
H^+ = proton,
a = total amount of the substance, in moles,
r = amount of R, the reduced form,
s = amount of S, the semi-oxidized form as semiquinone,
t = amount of T, the totally oxidized form,
d = amount of D, the semi-oxidized form as dimer,
x = equivalents of added oxidizing agent,
k = formation constant of the intermediate semiquinone form,

If the product, A^-, happens to be the ion of a weak acid it will tend to combine with a proton furnished either by the oxonium ion OH_3^+, if the solvent contains water, or by any other acid in Brönsted's generalized terminology:

$$A^- + H^+ \rightleftharpoons AH \tag{2}$$
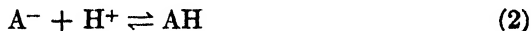
$\kappa =$ dismutation constant $= 1/k$,

$\gamma = 4\kappa - 1 = \dfrac{4-k}{k}$

$\xi = \dfrac{x}{a}$

$\mu = \xi - 1 = \dfrac{x-a}{a}$

$\lambda = 1 - \mu^2$

$\tau = \dfrac{t}{s}$

$\rho = \dfrac{r}{s}$

$q = \sqrt{1 + \gamma\lambda} = \sqrt{1 + (4\kappa - 1)(1 - \mu^2)}$

$E =$ potential,

$E_m =$ mean normal potential,

$E_1 =$ normal potential of the lower step,

$E_2 =$ normal potential of the higher step,

$E_i = E_{(\text{at }50\% \text{ oxidation})} - E_{(\text{at }25\% \text{ oxidation})} =$ index potential,

$K_1, K_2 =$ the two ionization constants of a bivalent acid,

$RT =$ product of gas constant and absolute temperature (printed in italics, in distinction to the above R and T),

$v =$ volume of solution containing total substance, a,

$Q = \dfrac{vd}{rt}$

$G = \dfrac{vd}{s^2}$

$L = \dfrac{Qa}{v}$

$\delta =$ slope of titration curve at midpoint where $\mu = 0$,

$N = t/r = 10^{\frac{\Delta E}{0.03}}$

$\alpha = \dfrac{E_i F}{RT}$

$k' = \dfrac{K_1}{K_2}$

ΔE is the difference between any observed potential and the midpoint potential.

If these two processes occur simultaneously the net effect can be represented by the combined reaction:

$$A + \epsilon + H^+ \rightleftharpoons AH \tag{3}$$

or

$$A + H \rightleftharpoons AH \tag{3a}$$

Only in such a case is the term "reduction" entirely equivalent to hydrogenation.

Exactly the same argument applies to the bivalent oxidation–reduction process of a substance B when the two steps occur simultaneously.   The corresponding reactions are:

$$B + 2\epsilon \rightleftharpoons B^{--} \tag{4}$$

$$B + 2\epsilon + 2H^+ \rightleftharpoons BH_2 \tag{4a}$$

$$B + 2H \rightleftharpoons BH_2 \tag{4b}$$
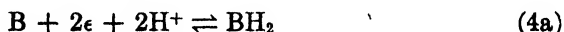
There are other variations in the form in which these reactions sometimes need to be written.   For example, the reduction of an ester is represented by:

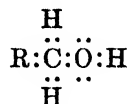$$RCOOEt + 2\epsilon + H^+ \rightarrow RCHO + (OEt)^- \tag{5}$$

However, the common feature of all these equations and the essential characteristic of the reduction process is that the compound undergoing reduction accepts electrons, as expressed in equations 1 and 4.   This process may be, and in most cases is, accompanied by changes in the condition of ionization of products first formed.   That is to say, the product resulting from reaction 1 or 4 may immediately attach or detach protons or hydroxyl ions, depending on its acidity and on the medium in which it is formed.   Any such changes in state of ionization, although usually accompanying the reduction, must be kept logically distinct.   It is often convenient to write reduction reactions in the forms of equations 3a or 4b, but for the purposes of developing a unified and consistent theory and a set of equations to describe the electrochemical facts of reduction, equations 3a and 4b must be thought of as broken into the two parts represented by equations 1 and 2.

A few examples will illustrate this idea.   Consider the reduction of an aldehyde.   The electronic structures corresponding to equation 4 are:
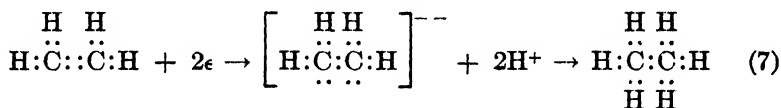
$$R{:}C{::}\ddot{O}{:} + 2\epsilon \rightarrow \left[R{:}\ddot{C}{:}\ddot{O}{:} \right]^{--} \tag{6}$$
$$\ddot{H} \qquad\qquad\qquad \ddot{H}$$
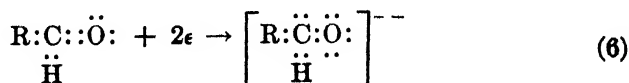
The product formed would be the divalent ion of an unmeasurably weak acid and would immediately attach protons to form the alcohol:

$$\text{R:}\overset{\overset{\textstyle H}{\cdot\cdot}}{\underset{\underset{\textstyle H}{\cdot\cdot}}{\text{C}}}\text{:}\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}\text{:H}$$
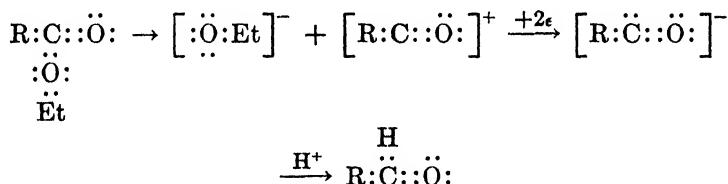
But this addition of protons has nothing to do with the reduction process, which is entirely contained in equation 6.

A similar case is afforded by the reduction of ethylene to ethane, in which the reduction and proton-attaching processes are:

$$\overset{\textstyle H\ \ H}{\text{H:}\overset{\cdot\cdot}{\text{C}}\text{::}\overset{\cdot\cdot}{\text{C}}\text{:H}} + 2\epsilon \rightarrow \left[\overset{\textstyle H\ H}{\text{H:}\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{C}}}\text{:}\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{C}}}\text{:H}}\right]^{--} + 2H^+ \rightarrow \overset{\textstyle H\ H}{\underset{\underset{\textstyle H\ H}{\cdot\cdot\ \cdot\cdot}}{\text{H:}\overset{\cdot\cdot}{\text{C}}\text{:}\overset{\cdot\cdot}{\text{C}}\text{:H}}} \quad (7)$$

The pairs of molecules AH and A^- or BH_2 and B^{--} of equations 2 and 4 may be said to be two states of ionization of the same acid, of which the ionized form in some cases may be practically incapable of existence.

Other cases also arise in which the ionization process involves hydroxyl or alkoxyl ions instead of protons. For example, the reduction represented by equation 5 can be written electronically:

$$\underset{\underset{\textstyle Et}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}\text{:}}}{\text{R:C::}\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}\text{:}} \rightarrow \left[\text{:}\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}\text{:Et}\right]^- + \left[\text{R:C::}\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}\text{:}\right]^+ \xrightarrow{+2\epsilon} \left[\text{R:}\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{C}}}\text{::}\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}\text{:}\right]^-$$

$$\xrightarrow{H^+} \overset{\textstyle H}{\text{R:}\overset{\cdot\cdot}{\text{C}}\text{::}\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}\text{:}}$$

In this case the attachment of the electron pair and the detachment of the ethoxyl group may occur simultaneously, but again the latter is an ionization step and must not be confused with the reduction itself.

In what follows equations 1 and 4 are considered as the elementary reduction process. The changes represented by equations 2, 3, 3a, 4a, and 4b contain features not belonging to the process proper of oxidation–reduction.

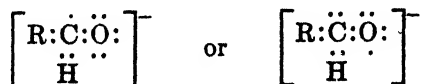## II. STEPWISE REDUCTION AND THE EXISTENCE OF FREE RADICALS

Usually in organic compounds reduction is bivalent, that is, it involves taking up two electrons, as represented in equation 4. This is because almost without exception the compounds which have been considered as stable organic molecules contain an even number of electrons. But it now appears that there is no reason why this must be so. In carrying out the

reduction represented by equation 4, by gradually adding a reductant to B, the process may take place in steps:
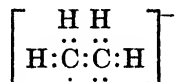
$$B + \epsilon \rightleftharpoons B^- \tag{8}$$

$$B^- + \epsilon \rightleftharpoons B^{--}$$
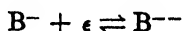
In the reduction represented by equation 4 each molecule of B takes up two electrons simultaneously and only two molecular species, B and B^{--}, are involved in the equilibrium. In the reduction represented by equation 8, however, each molecule of B first takes up one electron to form B^-. When such a reduction is performed by titrating with a reducing agent, three molecular species, B, B^-, and B^{--}, will be present in equilibrium with each other. It is a detailed analysis of this equilibrium which is one of the major objects of this review. From simple mass law equations, functions are derived which express the amounts of B, B^-, and B^{--} present at successive stages throughout such a reduction. One of the consequences of the existence of this equilibrium is that it is in general impossible to isolate the intermediate form or even to study it alone in solution. It is an essential property of these intermediate oxidation levels that they are always in a mobile equilibrium with the compounds on the next higher and the next lower step of oxidation, whereas ordinary valence-saturated organic compounds are usually inert with respect to establishing equilibria with other valence-saturated compounds. Acetaldehyde does not dismute to ethyl alcohol and acetic acid in an acid or neutral solution, although it would be possible, speaking purely thermodynamically. In contrast, the establishment of the equilibrium of a radical of the type mentioned with an electron donor or acceptor is just as unhampered as that of an acid or base with a proton donor or acceptor. If a large part of B is converted to B^- before B^- begins to accept electrons to form B^{--}, then the two steps of reduction of equation 8 will be separated. But if B^- begins to accept electrons while much B is left, then the steps will be said to overlap. In the reduction represented by equation 4 the overlapping is complete, and equation 4 is a limiting case of equation 8.
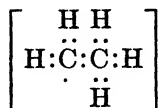
If B is a common organic molecule such as an aldehyde or a quinone it will have an even number of electrons and so B^- must have an odd number. For example, if the reduction of the aldehyde in equation 6 were to proceed in separated steps, it would be necessary to consider the existence of molecular species such as:

$$\left[R\!:\!\overset{\cdot}{\underset{\cdot\cdot}{C}}\!:\!\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}\!: \atop \underset{\cdot\cdot}{H} \right]^- \quad \text{or} \quad \left[R\!:\!\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}}\!:\!\overset{\cdot\cdot}{\underset{\cdot}{O}}\!: \atop \underset{\cdot\cdot}{H} \right]^-$$

Likewise, the intermediate step in the reduction of ethylene (equation 7) would have to be

$$\left[\begin{matrix} \text{H} \ \ \text{H} \\ \text{H}\!:\!\overset{..}{\underset{.}{\text{C}}}\!:\!\overset{..}{\underset{..}{\text{C}}}\!:\!\text{H} \end{matrix} \right]^{-}$$

or, on adding a proton,

$$\left[\begin{matrix} \text{H} \ \ \text{H} \\ \text{H}\!:\!\overset{..}{\underset{.}{\text{C}}}\!:\!\overset{..}{\underset{..}{\text{C}}}\!:\!\text{H} \\ \text{H} \end{matrix} \right]$$

that is, the ethyl radical would be the result. These particular radicals are not capable of existence to any measurable extent as components of equilibrium systems, at least not at ordinary temperatures. However, the compound of styrene and sodium probably has some such structure.

Outside the gas phase studies, there have been two approaches from which free radicals have been considered in the past. The first deals with actual isolation of radicals and determination of their molecular weights as shown, for example, in the extensive studies on compounds of the types of triphenylmethyl, diphenylnitrogen, triphenylhydrazyl, or diphenylnitric oxide. Radicals of these types have rarely been studied in aqueous solutions, because they are often very unstable in water. In organic solvents the equilibria involved in the combination of such radicals with themselves (dimerization) or with other radicals have been studied. On the other hand, reactions of such radicals to form simultaneously molecules of a higher and a lower oxidation level (dismutation), although known to occur, have not been so extensively studied.

The second approach to a study of free radicals included both organic and inorganic radicals and applies to such radicals in aqueous solutions; on the other hand, the studies are not on equilibrium systems and the existence of the radicals is not based on such direct evidence. Radicals of this sort are discussed by Franck and Haber (5) and by Haber and Willstätter (7, 6). As an example of the type of system studied, there is the oxidation of sulfurous acid by oxygen catalyzed by copper ion. Radicals are postulated as the primary molecular species formed. They are supposed to have a very short life time, since they are either oxidized or reduced immediately as they arise, or they are supposed rapidly to undergo irreversible side reactions such as dimerization to valence-saturated compounds. The radicals are members of a chain of reactions which may break sooner or later according to conditions and so lead to different final states of the system. The formation of the radical is supposed to require a considerable activation energy, and the course of the process depends on

kinetic factors. Thus the existence of radicals as intermediate steps in bivalent oxidations is studied, but the reactions considered are not sequences of continuously shifting thermodynamical equilibria but are in part irreversible processes.

The experimental basis on which the semiquinone theory is built supplies a new method for the study of radicals. Semiquinones are free radicals. They also frequently happen to be ions, because the substances dealt with have acid–base properties. They are stable molecules existing as intermediate oxidation levels in thermodynamic equilibrium in reversible bivalent reductions in aqueous solution. A measure of their stability is afforded by the steadiness of the electric potentials which can be obtained in systems of which they are components at precious metal electrodes. That such odd electron molecules can be stable is no more surprising than the stability of many other organic radicals whose radical nature is based on direct determinations of molecular weight. Direct determination of the molecular weight of semiquinones by any of the usual methods is in general not possible, since they exist in equilibrium with their oxidized and reduced forms.

Most of the substances in which semiquinone formation has definitely been shown to occur to a well-measurable extent are aromatic or heterocyclic compounds. In all cases the reduction can be interpreted as the stepwise addition of two electrons to atoms at the ends of a system of conjugated double bonds. The atoms at the ends of this system are usually oxygen or nitrogen atoms. In the first case the semiquinone level is favored in alkaline solutions, and in the second case it is favored in acid solutions. In all such examples the stability of the odd electron semiquinone molecule is due to the formation of a more or less symmetrical resonance system. It seems likely that the reason the formation of semiquinones has so far been observed only in molecules containing a conjugated system of double bonds is that such a system can act as an electron reservoir or electron "buffer". In accepting a single electron there exist a number of different ways of rearranging the whole electronic system of the molecule to accommodate the added electron. In each such arrange-ment of the electrons one atom of the conjugated system must be associated with an odd number of electrons. If the structure of the molecule is symmetrical, or at least nearly symmetrical, the odd electron may be imagined to oscillate between the two symmetrical moieties, just as the electron of the hydrogen molecule ion, resulting in resonance, which has been recognized, since Heisenberg's work, as a stabilizing factor.

On the other hand, consider the reduction of a simple aldehyde as represented by equation 6, or of a simple ethylenic compound as represented by equation 7. Such molecules might similarly be imagined to accept

electrons singly, giving rise to the radicals represented on page 8. Owing to lack of symmetry, there is a smaller chance of stability. This is just a general principle which we cannot yet survey in detail. Even without such a symmetrical structure, intermediate oxidation levels might still exist in concentrations extremely low indeed, but sufficient to play an important rôle in the kinetics of oxidation–reduction reactions.

III. DISMUTATION AND DIMERIZATION

The reaction $2B^- \rightarrow B + B^{--}$ will be referred to as dismutation. This is analogous to the Cannizzaro reaction or disproportionation, insofar as a given molecular species gives rise simultaneously to a higher and a lower state of oxidation. But in the Cannizzaro reaction both the oxidation and the reduction are bivalent as in the case of an aldehyde, considered in its hydrated form:

$$2R \cdot CH(OH)_2 \rightleftharpoons R \cdot CH_2OH + R \cdot COOH$$
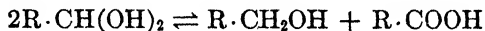
In a dismutation, on the other hand, the oxidation and reduction are univalent, such as might occur with the hypothetical radical, $R \cdot C(OH)_2$, namely:

$$2R \cdot C(OH)_2 \rightleftharpoons R \cdot CH(OH)_2 + R \cdot COOH$$

Among other reactions beside dismutation, which radicals can undergo, the process of dimerization is particularly important. In fact, triphenylmethyl is more usually looked upon as a dissociation product of its dimer, hexaphenylethane, than as an oxidation product of triphenylmethane. Although from the standpoint of classical organic chemistry dimerization is the most probable reaction for a radical to undergo, this reaction is not so general as was believed. It is true that radicals such as CH_3 easily dimerize rather than dismute. Furthermore, the first oxidation product of sulfhydryl compounds (hydrogen sulfide, sulfites, thiosulfates, and mercaptans) that can be detected is a disulfide:

$$2RSH \rightleftharpoons RSSR + 2H$$

This may be accounted for by assuming that a radical first forms which immediately dimerizes. Franck and Haber (5) presented good evidence for this assumption in the case of the oxidation of sulfurous acid.

Until quite recently the semiquinones seemed to differ from other known organic radicals in that the examples known showed no tendency to dimerize. There are two conditions which may account for this. In the first place, studies of the semiquinones have been made potentiometrically on aqueous solutions of electrolytes. To get titration curves that could easily be interpreted thermodynamically the work was always carried out in dilute solution, ranging from 10^{-3} to 10^{-5} molar. Such dilute solutions

are of course not favorable to the formation of dimers. In the second place, while the equilibria of dimerization of organic radicals have usually been studied in non-associated organic solvents, semiquinones are always studied in aqueous solution, which might favor the dissociation. However, there have recently been found several cases in which it has been possible to show that semiquinones can dimerize, and the extent of the dimerization has been measured (14, 19).

In general, a radical may be said to be capable of two kinds of reaction, —dismutation and dimerization. Sometimes the one prevails, sometimes the other. Unless the tendency to dimerize is very strong, as it is in the formation of disulfides, experimental conditions can be arranged to make the dimerization negligible. For, since dimerization is a bimolecular reaction, its extent depends on the concentration of the substances involved. At a sufficient dilution the dimerized form will practically completely dissociate into radicals. So, working in sufficiently dilute solutions, we can, as a rule, approach a condition where dimerization can be neglected (15, 19). Thus in what follows, if we sometimes speak of processes as if no dimerization occurred, we mean only that quantitatively it is negligible in comparison with dismutation.

A radical, of course, may be able to undergo various other chemical reactions, e.g., biphenylnitride can combine with nitric oxide. Such reactions need not be considered here at all. We always suppose that the system is exposed to no other chemical reagents than such as are just capable of changing its level of oxidation–reduction.

In what follows, those cases will be dealt with principally where dismutation is the only change to which the radical is subjected. This is the more fundamental situation. On the basis of the theory for this uncomplicated case, the adjustment of the theory to the case of dimerization can easily be presented in a short subsequent section. The first problem will be to express the equilibrium which exists among the three levels of oxidation–reduction whenever the substance is present in a not entirely oxidized or reduced state. For this purpose we imagine the mixture of which we are to study the equilibrium to be made up by partially oxidizing the reduced form. The gradual change of the level of oxidation–reduction of the system is imagined to be accomplished by titrating the reduced form with an oxidizing agent.

## IV. THE EQUILIBRIUM OF THE THREE LEVELS OF OXIDATION–REDUCTION

First we shall consider only what we have defined as the elementary process of bivalent oxidation–reduction. Suppose that there is given a solution of a substance in its reduced form and we titrate it with a strong oxidizing agent. Provided the potential range of the oxidizing agent is

much more positive than that of the substance to be oxidized, the following relations hold: Let the total molar amount of the substance, which is originally present in its reduced form, be a. Let the amount of the oxidizing agent added at a given stage of the titration be x, expressed in equivalents so that at the endpoint of titration $x = 2a$. At any point of the titration there will be a mixture of the reduced form R, of the semi-oxidized form, S, and of the totally oxidized form T. The molar amounts of these substances are designated by r, s, t. Then, at any point of the titration,

$$r + s + t = a \qquad (9)$$

$$s + 2t = x \qquad (10)$$

For the purpose of solving the equations for r, s, and t we need a third equation. This is given by considering the equilibrium

$$2S \rightleftharpoons T + R$$
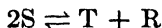
expressing the process of dismutation. The equilibrium of this reaction is

$$\frac{r \cdot t}{s^2} = \kappa = \frac{1}{k} \qquad (11)$$

κ will be designated as the dismutation constant. Its reciprocal value, k, will be referred to as the semiquinone-formation constant. We shall use either one or the other term according to convenience.

From equations 9, 10, and 11 we could express r, s, and t in terms of a, x, and κ. Since all molecules arising or disappearing during the titration are supposed to have the same molecular size and a dimerization reaction involving the formation of a bimolecular form is supposed not to occur, the absolute values of concentrations are irrelevant and only their ratios are significant. So it will be found more convenient to choose instead of the variables r, s, t and x, the set r/a, s/a, t/a and ξ where $\xi = x/a$. Then from equation 9,

$$\frac{r}{a} + \frac{s}{a} + \frac{t}{a} = 1 \qquad (12)$$

The solutions of these equations will be more symmetrical if a further substitution is made defined by the relation:

$$\mu = \xi - 1 \qquad (13)$$

This substitution places the zero point of the functions at the midpoint of the titration where ξ is equal to 1, which is a point of symmetry, instead of at the beginning of the titration where ξ is equal to zero. During the

titration μ varies from -1 to $+1$. A further substitution which will help to simplify the final results is:

$$\gamma = 4\kappa - 1 = \frac{4 - k}{k} \tag{14}$$

The solution of equations 9, 10, and 11 with the substitutions given in equations 13 and 14 then leads to the result:

$$\frac{r}{a} = \frac{1 - \mu}{2} - \frac{\sqrt{1 + \gamma(1 - \mu^2)} - 1}{2\gamma} \tag{15}$$

$$\frac{s}{a} = \frac{\sqrt{1 + \gamma(1 - \mu^2)} - 1}{\gamma} \tag{16}$$

$$\frac{t}{a} = \frac{1 + \mu}{2} - \frac{\sqrt{1 + \gamma(1 - \mu^2)} - 1}{2\gamma} \tag{17}$$

The functions r/a and t/a are antisymmetric in μ with respect to each other, since on changing μ for $-\mu$ either one becomes the other. The function s/a, on the other hand, is itself symmetric in μ, since changing μ for $-\mu$ does not change its value. The sum of the three functions is unity, as required by equation 12. The form in which these functions were written in the previous review (reference 9, p. 252) did not bring out the symmetry that exists among them and that is reflected in the symmetry of the experimental potentiometric titration curves. The older form of these functions has also the disadvantage that the choice of the sign before the square root depends on the value of k, whereas the present form is unambiguous. Purely mathematically, of course, there is a second series of solutions such that in equations 15, 16, and 17 a negative sign must be used before the square root. But such solutions have no physical significance. To show this the functions may be plotted for various assumed values of the parameter γ. When γ is any positive number the functions are ellipses, and when γ is a negative number they are hyperbolae. Physically, of course, negative values of γ are restricted to the range between -1 and 0. Physically also we are only interested in the segments of these functions in the range of μ between -1 and $+1$. In each case it will be found by actual plotting of the curves that of the two segments of each curve which fall within this physically significant range of μ, only that segment corresponding to the choice of the positive sign before the root of equations 15, 16, or 17 gives acceptable values of r/a, s/a, or t/a. The only physically acceptable values of these functions are positive values in the range of 0 to 1. Instead of plotting the functions direct consideration of the equations leads to the same conclusion. If it can be shown for one particular value of μ that the positive segment must

be chosen, this holds for all values of μ, since the function is continuous and cannot jump during the titration from one segment to the other. Let us take, for instance, $\mu = 0$, and consider equation 16. This then appears in the form

$$\frac{s}{a} = \frac{\pm\sqrt{1+\gamma}-1}{\gamma}$$

Since k is always a positive number, γ is always > -1. If γ is a positive number, the choice of the negative value of the square root would give a negative value for s/a; if γ is negative, s/a would become > 1 on choosing the negative square root. Neither of these values has any physical significance.

In the special case that $\kappa = \frac{1}{4}$, or $\gamma = 0$, these functions are useless, because they contain a term of the form $0/0$ and so are indeterminate. If, however, in equations 9, 10, and 11 we substitute for κ the value $\frac{1}{4}$ directly, the solution appears in the form:

$$\frac{r}{a} = \tfrac{1}{4}(1 - \mu)^2 \tag{18a}$$

$$\frac{s}{a} = \tfrac{1}{2}(1 - \mu^2) \tag{18b}$$

$$\frac{t}{a} = \tfrac{1}{4}(1 + \mu)^2 \tag{18c}$$

These latter functions are parabolic and have only one branch. As regards the manner of symmetry with respect to μ, the same holds as for equations 15, 16, and 17.

First formulation of the potential

Our main problem is to express the potential E as a function of x, or ξ, or μ. According to the principles of thermodynamics, the potential can be expressed in three different ways:

$$E = E_m + \frac{RT}{2F} \ln\frac{t}{r} \tag{19a}$$

or

$$E = E_1 + \frac{RT}{F} \ln\frac{s}{r} \tag{19b}$$

or

$$E = E_2 + \frac{RT}{F} \ln\frac{t}{s} \tag{19c}$$

E_m, E_1, and E_2 are constants characteristic of the particular chemical compound. E_m is the potential when $t = r$. It may be called the mean normal potential and is always the potential at the midpoint of titration, when $\mu = 0$. It is analogous to the normal potential of a bivalent oxidation–reduction system without step formation. E_1 is the potential at that point of the titration where $r = s$. It may be designated as the normal potential of the lower step. E_2 is the potential when $t = s$. It is the normal potential of the higher step.

To express E as a function of μ we could substitute the values of r, s, and t as obtained from equations 15, 16, and 17. The function resulting would be found awkward to manipulate in subsequent developments. We shall obtain more amenable forms in the following section. However, the equations 19 are useful for the following argument. Subtracting 19a and 19b, we obtain

$$E_m - E_1 = \frac{RT}{2F} \ln \frac{s^2}{rt}$$

or

$$E_1 = E_m - \frac{RT}{2F} \ln k \tag{20a}$$

and similarly

$$E_2 = E_m + \frac{RT}{2F} \ln k \tag{20b}$$

furthermore

$$E_m = \frac{E_1 + E_2}{2} \tag{21}$$

So it can be seen that the mean normal potential, E_m, lies halfway between E_1 and E_2. If two of the three potentials E_1, E_m, and E_2 are known, the third is also unambiguously defined.

Alternative formulation of the potential

Regarding equation 11, we can write it in a more symmetrical form by making the substitutions:

$$\frac{r}{s} = \rho$$

and

$$\frac{t}{s} = \tau$$

we then obtain

$$\rho\tau = \kappa \tag{22}$$

In order to introduce the variables ρ and τ instead of r and t in equation 9 and 10, we divide both by s and obtain

$$\rho + 1 + \tau = \frac{a}{s}$$

$$1 + 2\tau = \frac{x}{s}$$

To eliminate the remaining s, we divide the second of these two equations by the first:

$$\frac{1 + 2\tau}{1 + \rho + \tau} = \xi = \mu + 1 \tag{23}$$

Equations 22 and 23 are two equations for the two unknowns ρ and τ. By putting the value of ρ from equation 22,

$$\rho = \frac{\kappa}{\tau}$$

into equation 23 we obtain, writing only the solution with a positive sign before the square root,

$$\tau = \frac{1}{2(1 - \mu)} \left[\mu + \sqrt{\mu^2 + 4\kappa(1 - \mu^2)} \right] \tag{24a}$$

$$\rho = \frac{1}{2(1 + \mu)} \left[-\mu + \sqrt{\mu^2 + 4\kappa(1 - \mu^2)} \right] \tag{24b}$$

The other solutions, having a minus sign before the root, can be ruled out, for the absolute magnitude of the square root is always $> \mu$. Therefore both τ and ρ would be always negative on choosing the negative sign and so without physical significance. Now from equation 19a,

$$E - E_m = \frac{RT}{2F} \ln \frac{t}{r} = \frac{RT}{2F} \ln \frac{\tau}{\rho}$$

So we obtain

$$E - E_m = \frac{RT}{2F} \ln \frac{1 + \mu}{1 - \mu} + \frac{RT}{2F} \ln \frac{\sqrt{1 + \gamma(1 - \mu^2)} + \mu}{\sqrt{1 + \gamma(1 - \mu^2)} - \mu} \tag{25}$$

where, as before, γ stands for $(4\kappa - 1)$. This function shows the symmetry of the potential around the midpoint of titration quite clearly. By exchanging $+\mu$ for $-\mu$ we obtain a value for $E - E_m$ of the same absolute magnitude but with reversed sign. So the function is antisymmetric
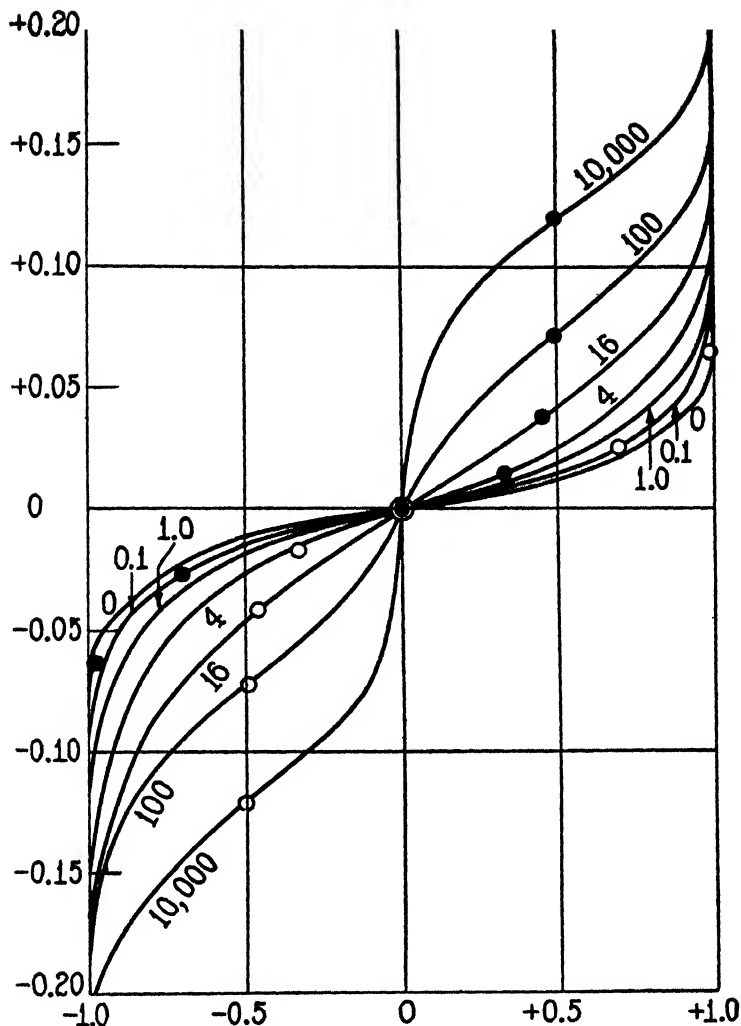
FIG. 1. Two-step titration curves involving formation of semiquinone radical. Abscissa: μ. $\mu = 0$ means 50 per cent of the total oxidation; $\mu = 1$ means 100 per cent of the total oxidation. Ordinates: $E - E_m$, the potential, referred to the mean normal potential E_m, in volts. Each curve holds for the value of k (semiquinone-formation constant) as indicated. White circle: that point of the titration curve where $E = E_1$ (the normal potential of the lower step). Black circle: that point where $E = E_2$ (the normal potential of the higher step). The black *and* white circle in the center belongs to the curve for $k = 1$; here E_m, E_1, and E_2 coincide at $\mu = 0$. White circles are on the left side for curves with $k > 1$; they are on the right side when $k < 1$. Both the white and the black circle in the curve for $k = 0$ belong actually to a curve for k intermediate between 0 and 0.1. When k is precisely 0, the circles would lie at $\mu = \pm 1$ and at potential $\pm \infty$. The lateral points of inflection begin to appear only when $k > 16$.

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with respect to μ. Another convenience of this equation is that the first logarithmic term is the one holding if no intermediate form arises. In this case, γ is very large and the second logarithmic term vanishes. The second logarithmic term is the correction due to step formation and the dismutation constant appears only in this term. This equation (equation 25) is also the most suitable for the differentiation which we will have to execute presently.

The shape of this function varies with the value of γ or from the relation 14 with the values of κ or k. Figure 1 shows the variation in shape for different values of k. If k is very small then the potential approaches the value

$$E - E_m = \frac{RT}{2F} \ln \frac{1 + \mu}{1 - \mu} \tag{26}$$

as it should be for a system with no intermediate step of oxidation.

When $\kappa = \frac{1}{4}$, or $\gamma = 0$ and $k = 4$, then

$$E - E_m = \frac{RT}{F} \ln \frac{1 + \mu}{1 - \mu} \tag{27}$$

a curve in which all ordinates are double the size of those in equation 26. This is the same curve as for a univalent oxidation system. These curves (equations 26 and 27) have a point of inflection at $\mu = 0$. When κ becomes much smaller, two more points of inflection appear. So a jump in the middle part of the curve appears which indicates a more distinct separation of the curve into two parts or two successive steps. For vanishingly small κ, or large k, these two points of inflection lie at $\mu = \pm\frac{1}{2}$. It is an important problem to study the existence and the location of these lateral points of inflection generally. This problem will be discussed by differentiation.

The first derivative of E

On differentiating E with respect to μ we obtain

$$\frac{dE}{d\mu} = \frac{RT}{F} \frac{1}{1 - \mu^2} \left(1 + \frac{1}{\sqrt{1 + \gamma(1 - \mu^2)}} \right) \tag{28}$$

When κ is not too small (say $> 10^{-2}$), the middle part of the potential curve where μ lies in the range from $+0.3$ to -0.3, is for all practical purposes a straight line. So it is very easy to determine graphically from an experimentally obtained curve the slope at $\mu = 0$. The slope, δ, at this point, is

$$\delta = \frac{RT}{F} \left(1 + \frac{1}{\sqrt{1 + \gamma}} \right) \tag{29}$$

In the special case that k becomes very small (or γ very large) this approaches the form:

$$\delta = \frac{RT}{F} = 0.02606 \text{ volt per unit of } \mu \tag{29a}$$

This is the slope of a titration curve in its midpoint (where $\mu = 0$), if no intermediate compound is formed.

On solving equation 29 for γ, we obtain

$$\gamma = \frac{1}{\left(\dfrac{F}{RT}\cdot\delta - 1\right)^2} - 1$$

or

$$4\left(\frac{F}{RT}\cdot\delta - 1\right)^2 \tag{30}$$

This equation serves to calculate k from the slope of a titration curve. Elema (4) has expressed this as follows: Draw the tangent at the midpoint of titration and extend it to intersection with the ordinate of the endpoint of titration. Read the magnitude of the ordinate at this point of intersection in volts. Subtract the voltage of the midpoint of titration. This difference equals δ (expressed in volts) and has the following relation to k, at 30°C.:

$$k = (76.63\delta - 2)^2 \tag{31}$$

The second derivative of E; points of inflection

From equation 28 we derive:

$$\frac{d^2E}{d\mu^2} = 2\frac{RT}{F}\cdot\frac{\mu}{\lambda}\left[\frac{1}{\lambda}\left(1 + \frac{1}{\sqrt{1 + \gamma\lambda}}\right) + \frac{\gamma}{2}\cdot\left(\frac{1}{\sqrt{1+\gamma\lambda}}\right)^3\right] \tag{32}$$

by first making the substitution:

$$\lambda = 1 - \mu^2$$

By equating this to zero we obtain the abscissae of the points of inflection. One such value directly evident from equation 32 is

$$\mu = 0$$

This gives the point of inflection at the midpoint of titration which is

always present independent of the magnitude of κ. Furthermore, by equating the term in brackets to zero, we obtain

$$q^3 + \frac{3}{2} q^2 - \tfrac{1}{2} = 0$$

where

$$q = \sqrt{1 + \gamma\lambda} \tag{33}$$

This equation of third degree in q has three real roots, of which two are alike and equal to -1, and the third is $\tfrac{1}{2}$. Only the latter root gives a result of physical significance. Retracing the definition of q back to the original variables (14, 33) we find that when q is $\tfrac{1}{2}$,

$$\mu = \pm \frac{1}{2} \sqrt{\frac{16\kappa - 1}{4\kappa - 1}} \tag{34a}$$

or, in terms of k,

$$\mu = \pm \frac{1}{2} \sqrt{\frac{k - 16}{k - 4}} \tag{34b}$$

Only when $k \geqq 16$ is μ real, and then it must lie in the range of μ from $-\tfrac{1}{2}$ to $+\tfrac{1}{2}$.

When $k < 16$, no acceptable solutions can be obtained. For, when $k < 16$ but > 4, μ is imaginary; and when $k < 4$, μ will always lie outside the range from -1 to $+1$. In neither of these cases have the solutions any physical significance. Furthermore, when the root $q = -1$ is chosen, the corresponding values of μ are found to be ± 1. But at these values of μ the potential is $\pm \infty$, and at values of μ greater than 1 or less than -1, the potential assumes complex values. So the vanishing of the second derivative cannot have the significance of a point of inflection.

The physically significant results can be summarized as follows: There is always one point of inflection at $\mu = 0$. Only when $k > 16$ are there two more lateral points of inflection, symmetrically situated at either side of the midpoint. As k increases from the value 16 the abscissae of these two lateral points of inflection move symmetrically from zero in a positive and negative sense and at large values of k approach the abscissae $\pm\tfrac{1}{2}$.

The fact that the threshold value of k is 16 was not recognized until recently (17). Both Elema and writers erroneously believed it to be 4, not having executed the necessary calculations and being misguided by the fact that the value 4 had been found to have another singular significance as discussed above (see equations 18).

Elementary and composite constants

All these considerations hold for the elementary process of oxidation–reduction as described by equations 8. To extend the theory to real conditions in which ionization phenomena appear we have to adapt the fundamental equations adequately. Equations 9 and 10 need not be changed at all if r means the amount of the R form in all its states of ionization, and similarly for s and t. Only equation 11 has to be modified. This equation holds for varying acidity only if we understand by r, s, and t the elementary forms B^{--}, B^-, and B. At any given pH the elementary B is a constant fraction of the total amount of B including such molecules also as BH^+, BH_2^{++}, etc., and the same holds for B^- and for B^{--}. Suppose then that as in equations 9 and 10 we allow r, s, and t to mean the total amounts of these several forms in all their states of ionization. The effect would be that k would be a constant only for a given pH and would vary with pH. Such a k is not a constant depending only on the chemical nature of the substance but is a parameter depending also on the hydrogen-ion concentration. The constant k or κ, such as is defined in equation 11, may be designated as the elementary constant, whereas this new parameter may be termed the effective constant. Experimentally only effective constants have been considered, so from now on we shall use the letters k and κ for effective constants. Then all our above considerations and formulas hold true. For a given oxidation–reduction system k may vary to an enormous extent with the pH depending on the ionization constants of each of the substances R, S, and T. The largest constant that has been observed is about 50 (9) (for oxyphenazine in very acid solution). The smallest that could be measured with satisfactory accuracy is about 0.05 (in lactoflavin at pH 4.6) (19). Many cases are now known for which in a certain pH range $k > 1$ and in another pH range $k < 1$. In general the curve for E_m as plotted against pH will not be parallel to those for E_1 or E_2. If k is unity, E_m, E_1, and E_2 coincide, and at this pH there is a crossing point of the three normal potential curves. But E_m for any one pH will always lie halfway between E_1 and E_2. When k becomes very small, say $<1/20$, the potentiometric method is no longer suitable for its precise determination. Practical methods for estimating k will be discussed later. Whenever $k < 1/20$, an error of, say, 1/10 of a millivolt in the index potential, or an exceedingly small error in the determination of the midpoint-tangent would involve a great error in the evaluation of k. In such a case it can only be recognized that k is very small. In fact, by this method all values of $k < 0.05$ are undistinguishable from $k = 0$. This situation prevails in many dyestuffs in ordinary pH ranges, and this is one of the reasons why the existence of a small amount of the intermediate radical has been overlooked until recently. Yet it might be foolish to disregard

a constant <0.05 just because the present potentiometric methods are unsuitable for its precise determination. It is much more likely that the difference in the magnitude of k in various systems is only a quantitative one and that the really simultaneous addition of two electrons in one step is not the common process in organic reduction, but an extreme limiting case which perhaps is never strictly realized. This is just about the opposite to what organic chemists have believed so far. We have to consider that, e.g., even for $k = 10^{-4}$, as much as $\frac{1}{2}$ per cent of the substance would be in the radical form at the half-reduced state. This follows from equation 49.

The location of E_1 and E_2 on the titration curve

On considering a titration curve it will be important to know at which point the potential equals E_m, at which point it equals E_1, and at which point it equals E_2. E_m is always the potential at 50 per cent oxidation, as is apparent from equation 25 on setting μ equal to zero, that is, $E_m = E_{\mu=0}$. Only when k is extremely large (>1000, say) is it easy to see that $E_1 = E_{\mu=-\frac{1}{2}}$ and $E_2 = E_{\mu=\frac{1}{2}}$. Generally, the location of E_1 and E_2 can be arrived at in the following way.

In order to locate E_1 we have to find that value of μ where $E = E_1$, that is to say, where r/a equals s/a. Equating the expression for r/a of equation 15 to that of s/a in equation 16, we obtain:

$$\mu_{E_1} = -\frac{k-1}{2k+1} \tag{35a}$$

In the same way, by equating equations 16 and 17, we obtain:

$$\mu_{E_2} = +\frac{k-1}{2k+1} \tag{35b}$$

This shows that for very large k we approach the limit:

$$\mu_{E_1} = -\tfrac{1}{2}$$
$$\mu_{E_2} = +\tfrac{1}{2}$$

For $k = 1$ we have

$$\mu_{E_1} = \mu_{E_2} = 0$$

In the latter case all three normal potentials coincide in the midpoint of titration.

For any $k > 1$, μ_{E_1} (that value of μ where $E = E_1$) is negative, and μ_{E_2} is positive. This may be designated as the natural order of the normal potentials. For any $k < 1$, μ_{E_1} is positive, and μ_{E_2} negative. This may

be said to be the inversed order of the normal potentials. For k approaching 0, this inversion is so complete that the normal potential of the higher step lies, in the limit, at the zero point of titration, i.e., at the point where only the reduced form exists, and the normal potential of the lower step at the endpoint of titration. In this limiting case the radical is incapable of existence and we have the completely overlapping bivalent oxidation which was formerly taken as the only possible case of bivalent oxidation in organic compounds.

V. THE PROBLEM OF DIMERIZATION

The entire analysis has so far been restricted to the case where the only molecular species intermediate between the oxidized form T and the reduced form R is the semiquinone radical S. This is the case which has been most thoroughly explored experimentally.

It has been pointed out earlier in this review that a semiquinone radical may dimerize to form a compound of double its molecular weight. Such a reaction may be represented by the equation:

$$2S \rightleftharpoons D \tag{36}$$
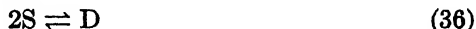
The same dimerization product could also be formed by combination of one molecule of the oxidized with one molecule of the reduced form of the given substance:

$$R + T \rightleftharpoons D \tag{37}$$

The dimeric molecule D is at the same oxidation level as the semiquinone molecule S. It will be shown in the subsequent analysis that the effect of the existence of such a dimeric molecule in equilibrium with the other molecules, R, S, and T, is to increase the slope of the titration curve at the midpoint. This is similar to the effect produced by semiquinone formation, as is evident from figure 1. Therefore methods must be found to decide in the case of a given titration curve with a midpoint slope greater than RT/F (equation 29a), whether this larger slope is due to semiquinone formation, dimerization, or a combination of both. General equations may be set up, analogous to equations 9, 10, and 11, to cover cases of both semiquinone formation and dimerization.

At any point of the titration curve we have

$$r + s + 2d + t = a \tag{38}$$

$$s + 2d + 2t = x \tag{39}$$

where x is the equivalent amount of the oxidizing agent. As before:

$$\frac{s^2}{rt} = k \tag{11}$$

In addition there are two equations for the equilibria 36 and 37.

$$\frac{vd}{s^2} = G \qquad \text{(``constant of dimerization'')} \tag{40}$$

$$\frac{vd}{rt} = Q \qquad \text{(constant of ``dimeric formation'')} \tag{41}$$

where v is the volume of solution containing the total amount of substance, a. The last three equations are of course not independent, the three equilibrium constants being related by the equation:

$$k \cdot G = Q \tag{42}$$

The general solution of this set of equations in terms of r, s, d, and t is, however, so complicated as to be quite impractical. But there is another special case which has been realized in practice and which can be subjected to analysis. This is the case where the semiquinone radical is completely or almost completely dimerized. One example (15) is phenanthrene-quinonesulfonate in acid solution. In this case during a titration there are only three molecular species which need to be considered in equilibrium, that is R, D, and T. Neglecting s we have from equations 38, 39, and 41:

$$r + 2d + t = a \tag{43}$$

$$2d + 2t = x \tag{44}$$

$$vd = Qrt \tag{41}$$

This set of equations is analogous to the set 9, 10, and 11, which formed the basis of the analysis of the case in which semiquinone formation occurs but dimerization is negligible. There is an important difference in the two sets of equations. It is this difference which must be responsible for the difference in the two titration curves derived from the two sets of equations. Equation 11 is homogeneous in the three variables r, s, and t, but equation 41 is not homogeneous in r, d, and t. It is thus not possible to set up the equation for the potential in terms of variables analogous to ρ and τ as was done in equations 22 to 25. However, solving equations 43, 44, and 41 for r and t and substituting these values in equation 19a, it is found that:

$$E = E_m + \frac{RT}{2F} \ln \frac{L\mu - 1 + \sqrt{L(L\mu^2 + 2) + 1}}{-L\mu - 1 + \sqrt{L(L\mu^2 + 2) + 1}} \tag{45}$$

in which

$$L = \frac{Qa}{v}$$

In figure 2 are plotted a series of curves analogous to those of figure 1. For large values of L step formation occurs as in the case of semiquinone formation with large k. The important difference between the two cases
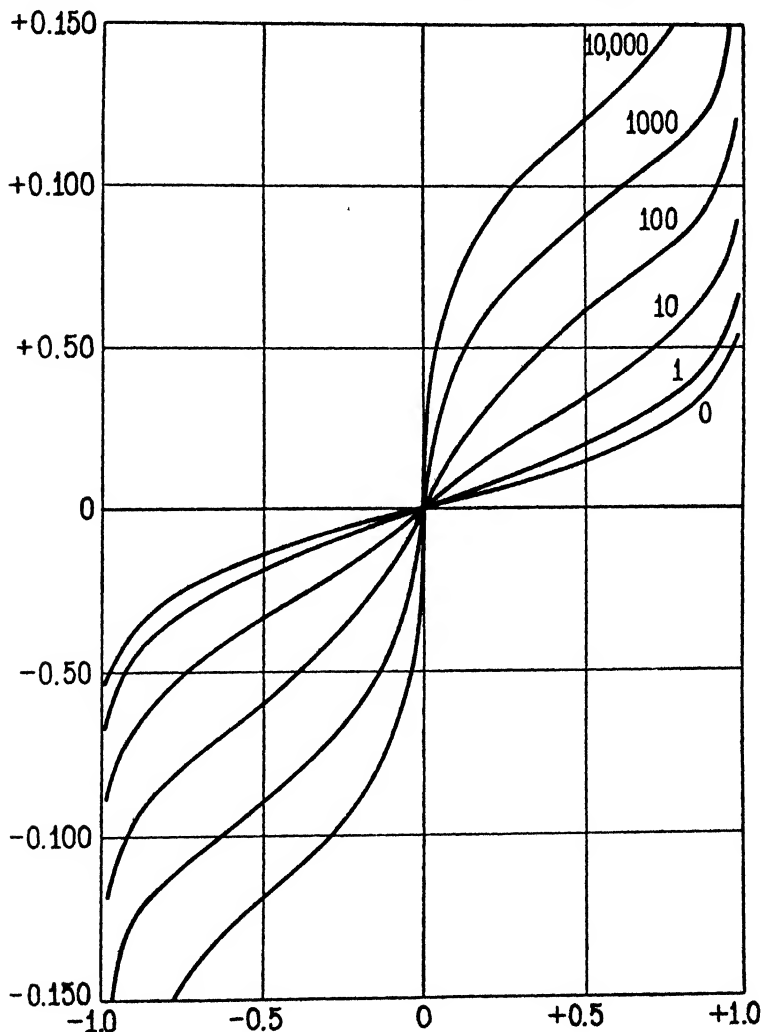

FIG. 2. Two-step titration curves involving formation of the dimeric intermediate compound alone. Abscissa and ordinates as in figure 1. Each curve holds for the value of L as indicated. $L = Q \times a/v$, the product of the dimeric formation constant and the molar concentration of the substance. Theoretically the two lateral points of inflection appear when $L > 4$. The figure shows that even for $L = 10$ these points of inflection are scarcely noticeable.

is that while the semiquinone curves are independent of concentration the dimer curves vary with the concentration of the substance titrated. This is evident since the particular curve obtained depends on

$$L = \frac{Qa}{v}$$

which varies directly with the concentration.

There is another difference between the semiquinone curves of figure 1 and the dimer curves of figure 2. It was shown that the abscissae of the lateral points of inflection of the semiquinone curves for large values approached the values $\mu = \pm 0.5$. In the case of the dimer curves (45) it can be shown by similar methods that when L is very large the abscissae of the lateral points of inflection approach $\mu = \pm\sqrt{2(3 + 2\sqrt{2})} = \pm 0.586$. Thus while the semiquinone curves for high values of k can be broken into two parts, each of which is symmetrical around its own midpoint, the dimer curves for high values of L separate into two parts each of which is an unsymmetrical curve. The two lateral points of inflection appear only when $L > 4$.

However, it must be emphasized that although these differences between the two families of curves can be deduced from an examination of the potential equations, if one had only a single titration curve at hand it would be difficult or practically impossible to decide whether it belonged to the semiquinone family or the dimer family. The more general case in which both semiquinone and dimer formation occur would of course lie in between the two special cases discussed.

VI. THE ANALYSIS OF EXPERIMENTAL CURVES, AND THE DETERMINATION OF CONSTANTS

A single titration curve can be interpreted only if the midpoint slope is accurately RT/F (equation 29a). In this case it can be said that neither semiquinone nor dimer formation occurs to an extent greater than about 1 or 2 per cent.

In practice there is an easier criterion than the midpoint slope, namely, the index potential, E_i, which is defined as the potential difference between 50 per cent oxidation and 25 per cent (or 75 per cent) oxidation, or the difference of the potential at $\mu = 0$ and $\mu = \pm\frac{1}{2}$;

$$E_i = E_{50\%} - E_{25\%} = E_{75\%} - E_{50\%}$$

or

$$E_i = E_{\mu=0} - E_{\mu=-\frac{1}{2}} = E_{\mu=+\frac{1}{2}} - E_{\mu=0}$$

In the limiting case, with no intermediate compound formed, $E_i = 0.0143$ volt at 30°C., for the ratio of r to t equals 3 at this point, and so

$$E_i = \frac{RT}{2F} \ln \frac{3}{1} = 0.0143 \text{ volt at } 30°C.$$

If an index potential greater than 14.3 millivolts is found, it must first be determined whether this is due to semiquinone formation, dimer formation, or both. From the analysis of the preceding section it is clear that the simplest test is to run a series of titrations at different total concentrations, a/v, of the substance titrated. If these curves are all identical when E is plotted against μ, then the only intermediate form is a semiquinone radical

Another test based on the same principle has been called the "dilution test" (11, 14). We designate the molar amount (not the concentration) of the totally oxidized form as t, that of the reduced form as r, and that of the intermediate, if it is a bimolecular meriquinone, as d. The equivalent of the equations 9, 10, and 11 is equations 43, 44, and 41. Solving for d we obtain:

$$d = \tfrac{1}{2}\left(a + \frac{v}{Q} \pm \sqrt{\left(a + \frac{v}{Q}\right)^2 + x(x - 2a)}\right)$$

So d depends on the volume v. If the color of D differs sufficiently from that of R and S, one can observe whether or not the maximum amount of D, as it exists at 50 per cent oxidation when $x = a$, will decrease with increasing volume of the solvent. If this is not the case, the intermediate compound is not a bimolecular meriquinone but a semiquinone radical. The variation of d with v may, however, sometimes be small and lie within the limits of error. This depends on the magnitude of v/Q. If this is $<< a$, the above equation approaches the form

$$d = \frac{x}{2} \quad \text{or } d = \tfrac{1}{2}(2a - x)$$

or, at 50 per cent oxidation when $x = a$, we obtain

$$d = \frac{a}{2}$$

and d is independent of the volume. If, however, $v/Q >> a$, the following equation is approximately fulfilled:

$$d = \frac{x(2a - x)}{4v}$$

and d will be inversely proportional to the volume. This is the condition best suited for the test. The amount of the unimolecular radical, s, would not depend on the volume at all, as shown by equation 16. It must be remembered that Q is what was previously called an effective constant and so in general varies with pH. So we have to choose a pH such that v/Q is very large in comparison with a. This is accomplished by choosing such a pH that the total amount of the intermediate compound at 50 per cent oxidation is so small as just to be noticeable. Since the color of the

intermediate form is in most cases much more intense than that of the R or T form, it is easy to detect even a very small amount of the intermediate form in a mixture with a large excess of the others. So, when at a properly chosen pH the dilution test shows that the total amount (not concentration!) of the intermediate substance is independent of the volume of the solvent, it is sufficient evidence that we have to deal with an S-form, not with a D-form.

This dilution test is very sensitive. Even if a precise colorimetry may be difficult, it is always easy to decide whether on increasing the volume tenfold the total amounts of the intermediate form are approximately unchanged, or tenfold decreased.

Thus it is possible either by running a series of titrations at different concentrations or by the application of the dilution test to decide whether the intermediate form consists only of a semiquinone radical. If this is the case then from the characteristics of the curve the semiquinone formation constant can be calculated. There are several ways to evaluate k from the experimental titration curve.

One method is based on equation 30 or equation 31. From the slope of the midpoint of titration k can be evaluated. This method is of value only when k is not too large and the slope not too steep. In the latter case the limits of error are rather great. So it should be used when the curves have no lateral inflection points at all, or at least when the jump in the middle part of the curve is not too great.

Another method is based on the determination of the index potential E_i. To express E_i as a function of k or κ, use is made of equation 25. By successively substituting the values $\frac{1}{2}$ and 0 for μ and finding the difference between the two resulting values of E we have:

$$E_i = \frac{RT}{2F}\left[\ln 3 + \ln \frac{\sqrt{1 + 12\kappa} + 1}{\sqrt{1 + 12\kappa} - 1}\right]$$

Let $\alpha = E_i F/RT$ and solve in terms of k instead of κ. Then:

$$k = (e^\alpha - 3e^{-\alpha})^2$$

or, at 30°C. and transferring to the base 10,

$$k = \left(10^{\frac{E_i}{0.06}} - \frac{3}{10^{\frac{E_i}{0.06}}}\right)^2 \tag{46}$$

Values of this function are tabulated in table 1 of the review (9). When E_i is large, say > 0.2 volt, equation 46 reduces to

$$\log k = \frac{E_i}{0.06}$$

The index potential method of determining k does not take full advantage of the titration curve, since only two points are used. To obtain a more accurate estimate of k a whole series of points of the experimental curve can be used to calculate the constant. In any bivalent titration curve, regardless of the form of the intermediate, we have the relation:

$$\Delta E = \frac{RT}{2F} \ln \frac{t}{r} = 0.03 \log \frac{t}{r} \qquad \text{(at 30°C.)}$$

where ΔE is the difference in potential at the midpoint of titration and at that point whose abscissa is x (which varies during the titration from 0 to 2a). Further, by setting $t/r = N$ this equation can be rewritten in the form

$$\frac{t}{r} = N = 10^{\frac{\Delta E}{0.03}} \tag{47}$$

Using this equation, together with the two equations,

$$r + s + t = a$$

$$s + 2t = x$$

we can solve for r, s, and t, giving

$$r = \frac{a - x}{1 - N}$$

$$s = \frac{x(1 + N) - 2Na}{1 - N} \tag{48}$$

$$t = \frac{N(a - x)}{1 - N}$$

From these values of r, s, and t in terms of the experimental variables of a titration curve it is possible to calculate k from equation 11 for a whole series of points of the curve.

It is an important problem to calculate the maximum amount of s which can arise during the titration. It is easy to see that the maximum amount of the S-form always exists at 50 per cent of the oxidation, when $\mu = 0$. This statement scarcely needs a proof, but it can be proved by differentiation of equation 16 with respect to μ. It is often of great importance to calculate this maximum amount, which of course depends on the value of k. Now, when $\mu = 0$,

$$r = t = \tfrac{1}{2}(a - s)$$

Then equation 11 appears in the form

$$\frac{(a - s)^2}{4s^2} = \kappa$$

which gives

$$\left(\frac{s}{a}\right)_{max.} = \frac{1}{1 + 2\sqrt{\kappa}} = \frac{\sqrt{k}}{2 + \sqrt{k}} \qquad (49)$$

If the tests outlined above indicate the existence of a dimeric compound, there are still two cases to distinguish. In the first case, case A, the dimeric form exists in measurable amounts but the amount of semiquinone is negligible and in the second case, case B, both semiquinone and dimer exist in measurable amounts.

Case A. In this case dimerization occurs but no appreciable semiquinone formation. The titration curves belong to the family of figure 2. Since s is very small, k cannot be calculated but can only be said to be less than 0.05, say. To show that a given curve belongs to this family it is necessary to run a series of curves at progressively higher dilutions. This is equivalent to decreasing L in the curves of figure 2. The limiting curve at sufficiently high dilution will be the usual curve for a two-electron change with no intermediate step and will have an index potential of 14.3 millivolts. Within a range of concentration which is low enough the form of this curve will not depend on concentration.

The dimer formation constant Q (equation 41) can be calculated from those experimental curves run at concentrations high enough so dimerization occurs. From the set of equations:

$$r + 2d + t = a$$

$$2d + 2t = x$$

$$\frac{t}{r} = N = 10^{\frac{\Delta E}{0.03}}$$

are found the values:

$$r = \frac{a - x}{1 - N}$$

$$d = \frac{x(1 + N) - 2Na}{2(1 - N)} \qquad (50)$$

$$t = \frac{N(a - x)}{1 - N}$$

From these Q can be calculated.

Case B. The last case to consider is the most general of all. It will be presented here not so much in accordance with one paper (15), but in the form shown in another paper (19), which is both easier and more general. During a titration both semiquinone and dimer are formed in appreciable amounts. In this case the shape of the curve is a composite of those of figures 1 and 2. The shape of the curve varies with concentration, but as curves are run at higher and higher dilution a limiting curve will be approached at which the dimerization becomes negligible and only the effect of semiquinone formation remains. At a dilution that is high enough the shape of the curve may be independent of concentration over a considerable range. In this range the curve has been designated as the "limiting curve for infinite dilution" and is one of the family of figure 1. This situation has already been experimentally realized in two cases (14, 19) and on further investigation may turn out to be quite common. In this case the constant k can be calculated from the limiting curve by the methods described for the simple semiquinone curves. With this constant determined it becomes possible to use the curves at higher concentration, where semiquinone and dimer are both formed, for the calculation of both Q and G. At these higher concentrations there are in equilibrium during a titration four molecular forms, R, S, D, and T. The amounts present at any point during a titration can be calculated from the equations:

$$r + s + 2d + t = a$$

$$s + 2d + 2t = x$$

$$\frac{t}{r} = N = 10^{\frac{\Delta E}{0.03}}$$

$$\frac{s^2}{rt} = k$$

From these it is found:

$$r = \frac{a - x}{1 - N}$$

$$s = \frac{(a - x)\sqrt{kN}}{1 - N}$$

$$d = \frac{x(1 + N) - 2aN - (a - x)\sqrt{kN}}{2(1 - N)} \tag{51}$$

$$t = \frac{N(a - x)}{1 - N}$$

From these values both Q and G, as defined in equations 40 and 41, can

be calculated from experimental curves and should be found constant both for different points of a particular curve and for a set of curves at different concentrations.

A glance at the expressions for r and t in the solutions (equations 48, 50, and 51) shows that in each case they have the same form. Since the potential can always be expressed by equation 19a it might appear that in all cases considered the potential curve would have the same shape. This is only so in appearance, however, since the expressions for r and t contain N, which from equation 47 is derived from the potential curve and carries in itself the difference in shapes of the curves of the three types discussed.

It may be emphasized in conclusion that we have always dealt in this review with systems in homogeneous solution. The decision whether a solid, crystalline quinhydrone is a radical, a dimer, or a compound of R and T in a ratio different from 1:1 requires entirely different methods. The very concept of molecular size, involving the decision between the assumption of a radical or a polymer, cannot simply be taken over from the theory of the dissolved state. The molecular size within a crystal is ambiguous. Which elementary unit, repeated periodically in a crystal, should be preferably considered as the molecular unit, can be decided in such a case only by measurement of the paramagnetic susceptibility. Although not the subject of this review, it may be emphasized that the method has been used successfully. In the crystalline state, in a number of cases, the paramagnetic susceptibility was that of a molecule with one magnetically unbalanced electron, in other cases it was smaller. In such a case, we might speak of a partial dimerization. It would, however, be more adequate, for the crystalline state, to speak about a state intermediate between unimolecular and bimolecular units, a resonance between two adjacent molecules, between a free and a combined condition.

VII. TWO-STEP ACIDIC DISSOCIATION

All these formulas, except those concerned with dimerization, can be easily extended to the field of ionization of bivalent acids. The theory of the titration curve for bivalent acids, especially with respect to the points of inflection, has been developed exhaustively by Auerbach and Smolczyk (1) in a very different way. It is, however, important to show that the method used in the present paper can also be extended to this problem in order to show the analogy between the problems of oxidation and of dissociation. It is gratifying to see that the results of that other method agree with what follows.

Consider a solution of a weak acid AH_2 at such a pH that it exists entirely in the form of the secondary ion A^{--}, and suppose that it is titrated with a strong acid. Then the anion will successively attach two protons.

$$A^{--} + H^+ \rightleftharpoons AH^-$$

$$AH^- + H^+ \rightleftharpoons AH_2 \tag{52}$$

Equations 52 are analogous to equations 8. At any point during the titration a pair of equations similar to equations 9 and 10 will hold good.

$$A^{--} + AH^- + AH_2 = a \tag{53}$$

$$AH^- + 2AH_2 = x \tag{54}$$
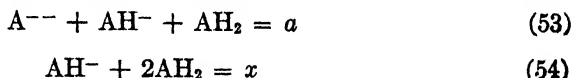
In this case a is the total amount of the weak acid in all its stages of ionization and x is the amount of strong acid added, in equivalents. To continue the analogy, the ion AH^- may be said to be in equilibrium with the other forms by a kind of "acidic dismutation":

$$2AH^- \rightleftharpoons AH_2 + A^{--}$$

and this equilibrium may be characterized by a constant analogous to the semiquinone formation constant:

$$\frac{[AH^-]^2}{[AH_2][A^{--}]} = k' \tag{55}$$

The more usual treatment of the equilibria in equation 52 is in terms of the two dissociation constants K_1 and K_2 defined by the relations:

$$K_1 = \frac{[H^+][HA^-]}{[HA_2]} \quad \text{and} \quad K_2 = \frac{[H^+][A^{--}]}{[HA^-]} \tag{56}$$

From equations 55 and 56 it is evident that

$$k' = \frac{K_1}{K_2} \tag{57}$$

Thus the three basic equations, 9, 10, and 11, of the semiquinone theory from which all subsequent formulas and relations were deduced are identical in form with a corresponding set, 53, 54 and 55, that could be used to develop the theory of the titration of dibasic acids. The equivalence of the two theories is established by this identity in form of the three basic equations and the relation (57) which shows the "acidic dismutation" constant k' to be the ratio of the classical ionization constants. In particular, it may be pointed out that the potentiometric titration curve of a dibasic acid has no jump in its middle section unless the ratio K_1/K_2 is greater than 16, a result which was obtained in a different way by Auerbach and Smolczyk (1) in 1924.

But although the physical pictures as described by equations 8 and 52 are so similar and the mathematical deductions from these equilibria are

identical there nevertheless appear to be fundamental differences between two-step oxidation and two-step ionization. The semiquinone formation constant of the two-step oxidation theory may assume any positive value between zero and infinity. The corresponding constant of the ionization theory given in equations 55 or 57 appears, however, practically never to be less than about 5.
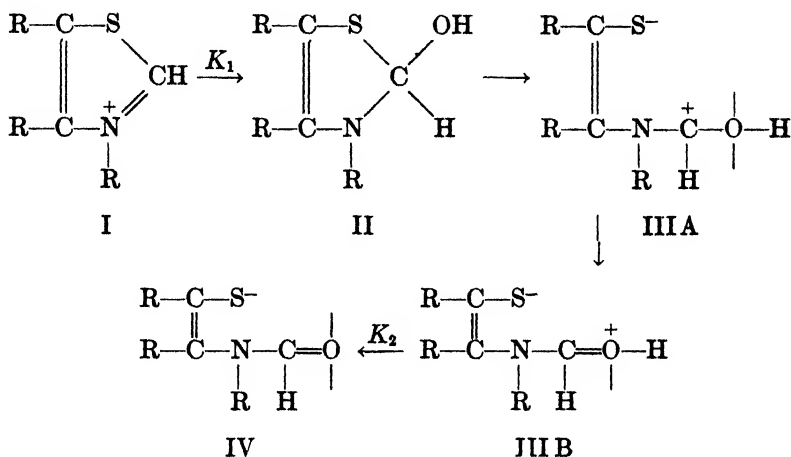
To understand this difference we must examine in more detail the effects of electron addition to a molecule as represented by equation 8 and of proton addition as represented by equation 52. Suppose we have the anion of a dibasic acid or, what is even more general, suppose we have a molecule which can accept two protons; the acceptance of one proton may be represented by equations such as:

$$A^{--} + H^+ \rightarrow AH^-$$
$$B^- + H^+ \rightarrow BH \qquad (58)$$
$$C + H^+ \rightarrow CH^+$$
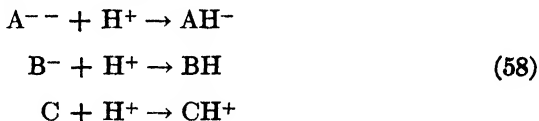
The acceptance of this proton may bring about a more or less profound rearrangement of the electrons of the molecule accepting the proton. Usually it does not. For example, if the doubly charged succinate ion accepts one proton it is probable that this does not greatly affect the electronic arrangement of the second carboxylate group. Actually, practically all studies of titration curves of dibasic acids have been of this type. In such cases each acid group functions independently and the only influence of one on the other is due to electrostatic forces. If the groups are widely separated in the molecule this electrostatic effect becomes small. In the further case that both acid groups are identical, as in the cases of dicarboxylic acids or diammonium salts, the statistical theory can be applied and it appears that K_1/K_2 approaches 4 as a lower limit, as shown by Wegscheider (23; see also 2). Such a limit is realized in practice in the titration of the two phenolic groups of phenolphthalein, which Thiel and Diehl (22) find to differ by approximately half a pH unit. In the case of molecules with such independently functioning acid groups it is of course necessary that K_1 be greater than K_2, merely because K_1 is defined as the greater constant.

It is, however, imaginable that the acceptance of a proton by a molecule such as shown in equation 58 may bring about a radical rearrangement of the electronic structure, resulting in the formation of a new molecule which could actually attach a proton more readily than the first molecule. In such a case K_2 would be greater than K_1 and k' of equation 57 would be less than 1. An example illustrating this already occurs in the literature, but now that the principle is realized additional ones may be discovered. The chemistry of this curious case was first described by Mills,

Clark, and Aeschlimann (20) and later shown to be generally true of thiazolium salts (3). A titration curve showing the lack of formation of any intermediate step of ionization was given by Williams and Ruehle (24) for 4-methylthiazolethiode. We may interpret this type of ionization as follows:

$$
\begin{array}{ccc}
\underset{\text{I}}{\begin{matrix} \text{R—C—S} \\ \| \quad\;\; \diagdown \\ \| \quad\;\; \text{CH} \xrightarrow{K_1} \\ \text{R—C—N} \\ \overset{+}{\underset{\text{R}}{|}} \end{matrix}}
&
\underset{\text{II}}{\begin{matrix} \text{R—C—S} \quad\;\text{OH} \\ \| \quad\;\; \diagdown\;\diagup \\ \| \quad\quad \text{C} \\ \| \quad\;\; \diagup\;\diagdown \\ \text{R—C—N} \quad\;\text{H} \\ \underset{\text{R}}{|} \end{matrix}}
&
\longrightarrow
\quad
\underset{\text{III A}}{\begin{matrix} \text{R—C—S}^- \\ \| \\ \| \\ \text{R—C—N}\overset{+}{-}\text{C—O—H} \\ \underset{\text{R}}{|}\;\;\underset{\text{H}}{|} \end{matrix}}
\end{array}
$$

$$
\underset{\text{IV}}{\begin{matrix} \text{R—C—S}^- \\ \| \\ \| \\ \text{R—C—N—C=O} \\ \underset{\text{R}}{|}\;\;\underset{\text{H}}{|} \end{matrix}}
\xleftarrow{K_2}
\underset{\text{III B}}{\begin{matrix} \text{R—C—S}^- \\ \| \\ \| \\ \text{R—C—N—C}\overset{+}{=}\text{O—H} \\ \underset{\text{R}}{|}\;\;\underset{\text{H}}{|} \end{matrix}}
$$

III is a zwitter ion with a negative charge at the sulfur atom and a positive charge either at the carbon atom or at the oxygen atom, as at III A or III B. In either case III is a very strong acid and at the pH prevailing at its formation is entirely converted to IV. Obviously K_2 is very much greater than K_1.

Turning now to the case of two-step reduction, it appears clear why values of k, the semiquinone-formation constant of equation 11 and the analogue of equation 55, may readily take on values less than unity. The acceptance by a molecule of a single electron necessarily brings about an electronic rearrangement, and because of the tendency of electrons to pair the resulting molecule may take up a second electron more readily. In such cases k is less than 1. That this is not always the case is clear, however, from the large number of cases now known where the semiquinone-formation constant is much greater than 1.

There is another respect in which the reduction reactions of equation 8 differ in practice from the ionization reactions of equation 52. This may be traced to what was defined early in this review as the elementary reduction process. Actually, as was subsequently pointed out, elementary reduction processes are generally complicated by simultaneous ionization processes, so a distinction had to be made between the elementary semiquinone-formation constant and the effective constant which is usually measured.

This circumstance can very easily cause the practical dismutation constant to become much smaller than 1, and even undistinguishable from 0, without resorting at all to the effect of electronic rearrangement mentioned before. In the field of ionization theory, however, the acceptance of protons is the analogue of the elementary reduction process. This is usually not complicated by any gain or loss of electrons. The reason for this is clear. Both oxidation–reduction and acid–base titrations are usually carried out in aqueous solution or in solvents such as acetic acid or alcohol which are similar in that they can act as acceptors or donors of protons. Solvents which can act as acceptors or donors of electrons are never used. So while oxidation–reduction titrations are complicated by acid–base equilibria, acid–base titrations are not complicated by oxidation–reduction equilibria.

REFERENCES

(1) AUERBACH, E , AND SMOLCZYK, E.: Z. physik. Chem. **110**, 65 (1924).
(2) BJERRUM, N.: Z. physik. Chem. **106**, 219 (1923).
(3) CLARKE, H. T., AND GURIN, S.: J. Am. Chem. Soc. **57**, 1876 (1935)
(4) ELEMA, B.: Rec. trav chim. **52**, 569 (1933); **54**, 76 (1935); J. Biol. Chem **100**, 149 (1933).
(5) FRANCK, J., AND HABER, F.: Sitzber preuss. Akad. Wiss. Physik. math. Klasse **1931**, 250.
(6) HABER, F.: Naturwissenschaften **19**, 450 (1931).
(7) HABER, F., AND WILLSTATTER, R.: Ber. **64B**, 2844 (1931).
(8) HILL, E. S : Proc. Soc. Exptl. Biol. Med. **35**, 363 (1936).
(9) MICHAELIS, L.: Chem. Rev. **16**, 243 (1935).
(10) MICHAELIS, L.: J. Am. Chem. Soc. **58**, 816 (1936).
(11) MICHAELIS, L.: J. Am. Chem. Soc. **58**, 873 (1936).
(12) MICHAELIS, L.: Trans. Electrochem. Soc. **71**, 107 (1937).
(13) MICHAELIS, L., BOEKER, G. F., AND REBER, R. K.: J. Am. Chem. Soc. **60**, 202 (1938).
(14) MICHAELIS, L., AND FETCHER, E. S.: J. Am. Chem. Soc. **59**, 1246 (1937).
(15) MICHAELIS, L., AND FETCHER, E. S : J. Am. Chem. Soc. **59**, 2460 (1937).
(16) MICHAELIS, L., REBER, R. K., AND KUCK, J. A.: J. Am. Chem. Soc. **60**, 214 (1938).
(17) MICHAELIS, L., AND SCHUBERT, M. P.: J. Biol. Chem. **119**, 133 (1937).
(18) MICHAELIS, L., SCHUBERT, M. P., AND SMYTHE, C. V.: J. Biol. Chem. **116**, 587 (1936).
(19) MICHAELIS, L., AND SCHWARZENBACH, G.: J. Biol. Chem. **123**, 527 (1938).
(20) MILLS, W. H., CLARK, L. M., AND AESCHLIMAN, J. A.: J. Chem. Soc. **123**, 2353 (1923).
(21) PREISSLER, P. W., AND HEMPELMAN, L. H.: J. Am. Chem. Soc. **59**, 141 (1937).
(22) THIEL, A., AND DIEHL, R.: Sitzber. Ges. Beförder. ges. Naturw. Marburg **62**, 472 (1927).
(23) WEGSCHEIDER, R.: Monatsh. **16**, 153 (1895).
(24) WILLIAMS, R. R., AND RUEHLE, A. E.: J. Am. Chem. Soc. **57**, 1856 (1935).

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